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**DEVELOPMENT AND THERMAL CHARACTERIZATION OF
CELLULOSE/CLAY NANOCOMPOSITES**

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Engineering Science
in

The Interdepartmental Program in Engineering Science

by
Christopher D. Delhom
B.S., University of New Orleans, 2000
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ABSTRACT

Cotton is the most important textile fiber for apparel use and is preferred to synthetic fibers for reasons such as comfort and feel. Cotton may also be used to produce the regenerated cellulose fibers, such as lyocell and viscose, which have numerous textile applications. A major drawback of cotton, and other cellulosic fibers, is its inherent ability to burn. Many finishes have been developed to impart flame resistance to cotton. These finishes have limited use in textiles for apparel due to problems with the finish not being durable during laundering and increasing the susceptibility of the fabric to wear. Most of these finishes have been developed for products that are not laundered, such as drapery and furnishing fabrics. The development of cellulose/clay nanocomposites for use as flame retardant materials based on cotton is reported in this paper. These materials are designed to take advantage of the thermal stability and flame resistance imparted by silicate filler materials and should require no fire retardant finish. The use of cellulose/clay nanocomposites can allow for the use of natural fibers in applications which are currently limited to synthetic fibers. The use of cellulosic fibers as a feedstock for the composite materials makes use of renewable resources and reduces the use of harsh chemicals normally found in flame retardant materials and finishes.

Novel nanocomposite materials have been produced from cellulose with layered silicate clays used as the nanofiller material. Three exfoliation and intercalation methods using different solvents and clay pretreatment techniques were attempted in production of these organic-inorganic hybrids. The method that resulted in superior cellulose/clay nanocomposites utilized a pretreatment of the clay and 4-methylmorpholine-*N*-oxide as the cellulose solvent. The nanocomposites show significant improvements in thermal properties when compared with cellulose control sources and cellulose processed under the conditions for nanocomposite preparation. The degradation temperature of the nanocomposites increased by 45 °C and the

char yields for some compositions doubled those of the controls. The crystalline melt of the materials decreased by 15 °C.

1. INTRODUCTION

1.1 Nanocomposites

Nanocomposites are an emerging class of composite materials. Composite materials can be divided into two general classes, fiber-reinforced (fibrous composites) and particle-reinforced (particulate composites). Particulate composites can be further divided into random orientation and preferred orientation composite materials, as shown in Figure 1.1.¹ Nanocomposites fall into the particulate composite classification. Nanocomposites are notable for their use of relatively small amounts of reinforcement material. Traditional composite materials make use of 10-20% reinforcement material. Nanocomposites can show significant improvement with additions of reinforcement material as small as 1-2%.

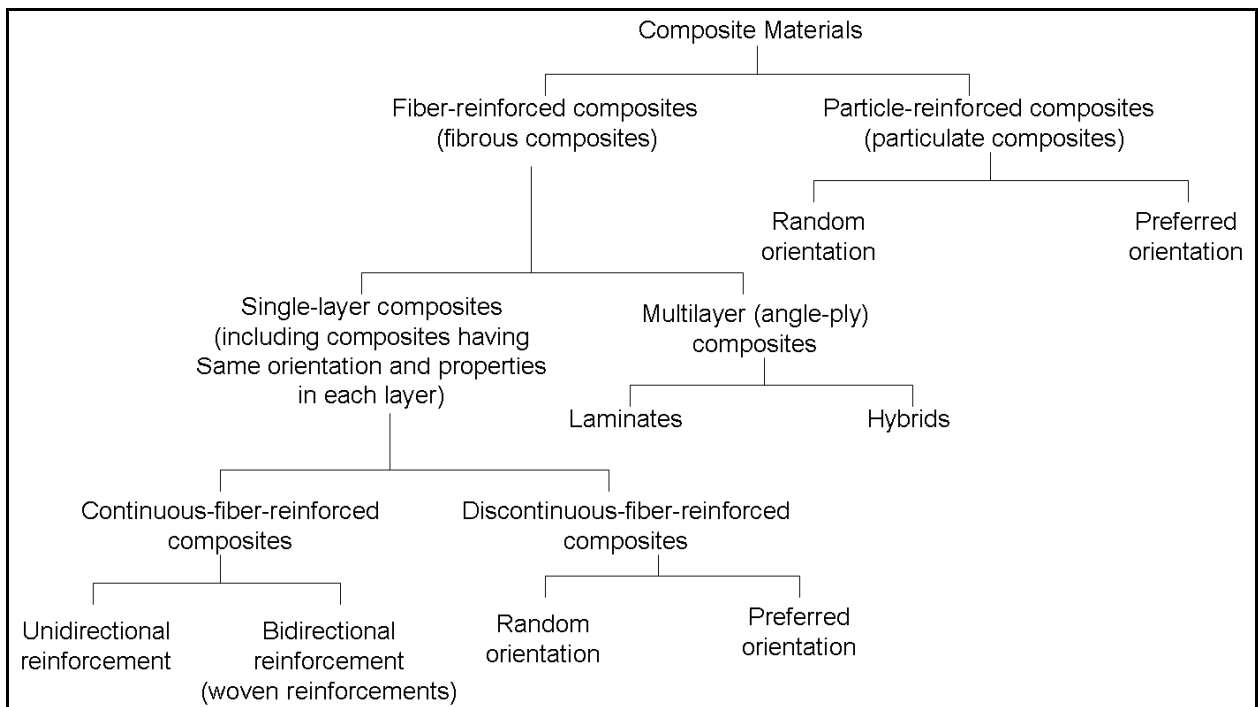


Figure 1.1 - Classification of Composite Materials¹

In order for a material to be considered a nanocomposite, the reinforcement material must have dimensions in the nano-scale. There are particulate composites which have reinforcement material on the micro-scale, these are known as microcomposites. Figure 1.2 illustrates the

differences between microcomposites and nanocomposites. Microcomposites may demonstrate similar properties and improvements to nanocomposites; however nanocomposites are generally more effective with less reinforcement material added to the matrix material. Polymer/clay nanocomposites may be either intercalated or exfoliated nanocomposites. The exfoliated nanocomposites have more complete separation of the silicate layers in the clay and are more effective.

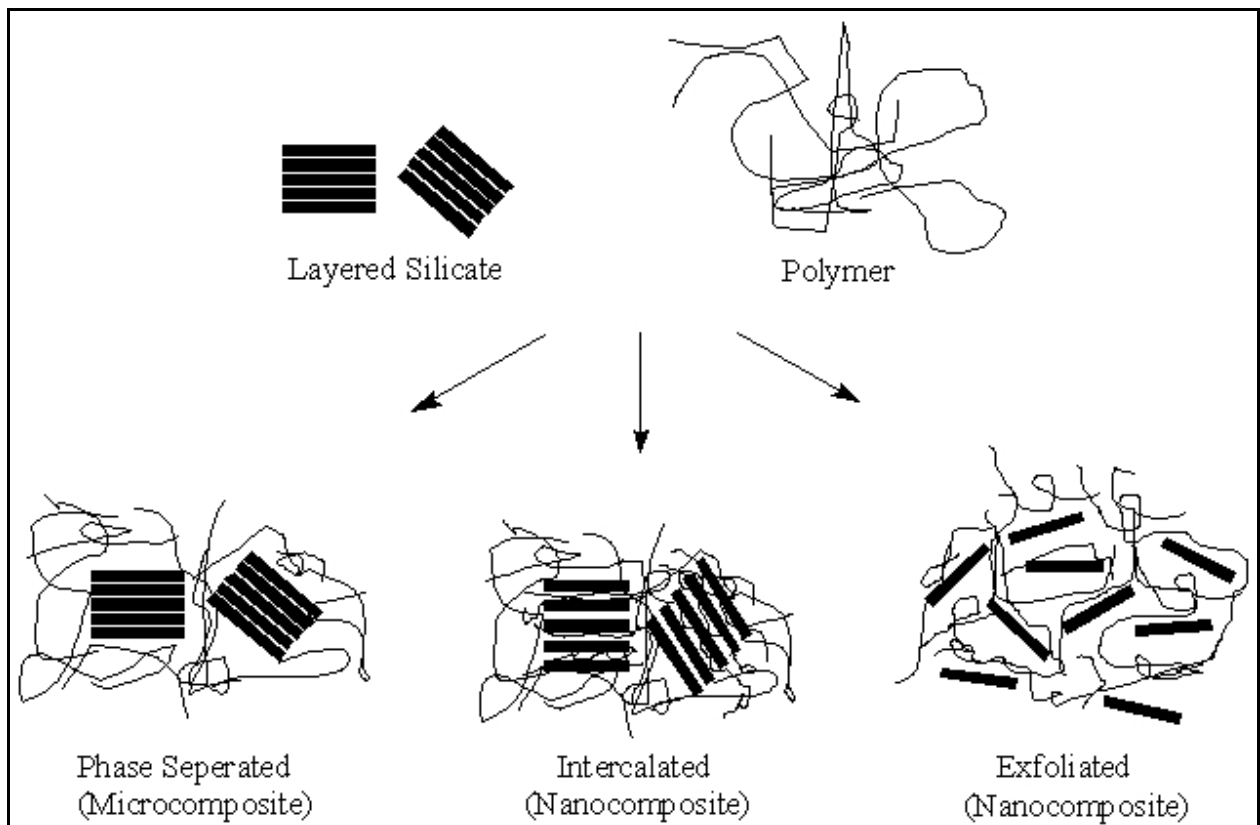


Figure 1.2 – Potential Particulate Composites

The clay materials consist of stacked silicate layers. These layers must be opened up in order to increase the interfacial contact between the polymer and clay. The layers are swollen and begin to separate in the nanocomposite formation process and the material is said to be intercalated. The ideal state is for the platelets to become so swollen and separated that they are no longer stacked. This condition is referred to as exfoliated (Figure 1.2). Incomplete

intercalation and exfoliation can lead to the formation of phase-separated microcomposites instead of the desired nanocomposites. Intercalated, but not exfoliated, nanocomposites are possible and are more desirable than microcomposites, however they are not as effective as exfoliated nanocomposites.

1.2 Polymer/Clay Nanocomposites

Polymer/clay nanocomposites consist of a polymer matrix reinforced with nanoparticles of clay. Nanostructured organic-inorganic composites are “mixed” on a near molecular level and behave much differently than conventional composites. These materials show large increases in performance properties with the addition of small amounts of inorganic filler material. Over the last 10-15 years there has been much research interest in polymer/clay nanocomposites. In most research the polymer matrix has been a synthetic polymer such as, but not limited to, polyamides², polyimides³, methacrylates^{4, 5}, and polystyrene⁶. The typical clay of choice for these composites is montmorillonite. Montmorillonite clay has a large surface area providing plenty of interfacial region in the nanocomposite. The large amount of interfacial region allows for an enhancement of thermal and tensile properties at low percentages of incorporation into the polymer matrix. The montmorillonite clay has an average length of 2000Å and width of 10Å. Research has shown that the clay must be pretreated before incorporation into the polymer matrix to ensure the formation of true nanocomposites.^{2, 7} The pretreatment of the clays is intended to separate the silicate layers to allow more thorough incorporation with the polymer matrix, as shown in Figure 1.2.

Although montmorillonite is the most commonly used clay, it is far from the only choice. Many different organic clay materials have been used in the production of polymer/clay nanocomposites. The most common clays, in addition to montmorillonite, are cloisite and kaolin. All of these clays are made up of silica sheets and contain extremely large aspect ratios.

The manufacturing of polymer/clay nanocomposites is a relatively straightforward process. Thermoplastic polymers, which the majority of research has been conducted on, are simply melted in advance of the addition of the nanoparticle filler materials. Thermoset polymers, such as cellulose, provide a bigger challenge. Thermoplastic polymers have a melting point lower than their degradation temperature. Thermoset polymers degrade at a lower temperature than their melting point and therefore may not just be simply melted. Thermoset polymers must be dissolved into a solution from which the polymer/clay nanocomposite may be reprecipitated after the polymer and clay become a homogeneously mixed solution. Thermoplastic polymers are simply allowed to solidify after incorporation of the nanoparticle filler material. The nanoparticles may also be used as nucleating sites during the solidification or reprecipitation process. This potentially allows for much finer control of the crystalline structure of the nanocomposite materials.⁸

1.3 Project Objective

Cotton is the most important textile fiber and is preferred over synthetic fibers and other natural fibers for reasons such as comfort and feel.⁹ Estimated global production of cotton for 2006/07 is 115.7 million bales of cotton. The United States is estimated to produce approximately 21.3 million bales of cotton.¹⁰ The economic impact of cotton production on the United States economy is estimated at over \$27 Billion for the 2006/07 crop year.¹¹ Cotton and other cellulosic fibers, such as kenaf, rami, and flax face stiff competition and shrinking market share due to synthetic fibers. Although cotton is the first choice for apparel, there are certain markets where natural fibers unable to compete with synthetic fibers.¹² Regenerated cellulose fibers, such as lyocell and viscose, have been developed to compete with synthetic fibers. Regenerated cellulose fibers may be produced using cotton or other sources of cellulose. One of the major drawbacks to cotton and current regenerated cellulose fibers is its inherent ability to

burn. Numerous chemical finishes have been developed to impart various levels of flame resistance to these fibers. These finishes have been successful but somewhat limited in application due to problems with the finish remaining on the material after laundering or wear and abrasion. Due to this limitation, many of these finishes are only used in applications which do not require laundering or expose the material to excessive wear such as draperies and furnishing coverings.^{13,14,15,16}

Literature reviews show the use of montmorillonite clays for filler in nanocomposite materials in which the matrix polymer are synthetic polymers have shown significant increase in thermal properties. Some work has been done with natural polymers; however they have been thermoplastic polymers such as cellulose acetate^{17, 18}. Other nanocomposite work with cellulose utilized cellulose “whiskers” as the reinforcement material and not as the matrix.^{19, 20, 21}

The objective of this project is to develop cellulose/clay nanocomposites for use as a flame retardant material based on cotton and other sources of cellulose. These materials should require no flame retardant finish.

1.4 Description of Project Work Plan

The challenges facing cotton are clear. The textile industry would be well served by the development of a new material possessing the positive attributes of cellulose fibers and yet not require the use of chemical flame retardant finishes. The work to develop such a material was performed according to the plan below.

1. Review existing literature about polymer/clay nanocomposites, regenerated cellulosic materials, and related technologies necessary to develop a regenerated cellulose/clay nanocomposite.
2. Perform laboratory work to determine the appropriate manufacturing method(s) to produce the desired nanocomposite material.

3. Produce candidate materials for testing.
4. Conduct appropriate tests to determine if the material produced is a true nanocomposite.
5. Conduct appropriate tests to determine if the material produced possesses enhanced thermal properties.
6. Develop methods to produce the nanocomposite material in a usable form.

1.5 Overview of Thesis

The challenges that cotton and other cellulosic fibers face is detailed in this first chapter. This first chapter also introduces the concepts of nanocomposite materials and the possibilities presented by polymer/clay nanocomposites. This chapter also includes the concept for a novel cellulose/clay nanocomposite material and a description of this thesis.

Chapter 2 describes the literature review of current polymer/clay nanocomposite research. This chapter also covers literature reviews of current methods for the dissolution and regeneration of cellulose materials.

Chapter 3 presents the various methods and materials used in attempts to create a flame retardant cellulose/clay nanocomposite. The chapter covers the development of all stages of production required for the manufacture of the desired material.

Chapter 4 reviews the testing that the novel material was subjected to for purposes of identifying its physical makeup. This chapter includes the results of those tests.

Chapter 5 reviews the testing, and subsequent results, which the nanocomposite material was subjected to for purposes of characterizing its thermal properties.

Chapter 6 provides a look at the various production steps involved in producing a useable material. This chapter includes the production of fibers for textile applications as well as other forms which the composite material may take.

Chapter 7 presents the conclusions from the project and recommendations for future work to scale-up the processing to an industrial stage and produce a commercially viable product.

2. LITERATURE REVIEW

2.1 Review of Cellulose Dissolution and Regeneration

The first regenerated cellulosic fiber was created via the viscose process and is commonly known as “rayon” or “viscose rayon”. A more recent process to create regenerated cellulosic fibers is known as the lyocell process and is commonly known by the trade name “Tencel”.

The viscose process was invented in the late 1800s and began to be marketed in the early 1900s. The process to create rayon is complex and requires a great deal of chemicals, most of which are not reusable or recycled. The process begins with dissolving cellulose in a caustic solution, such as sodium hydroxide (NaOH). The dissolved cellulose is exposed to carbon disulfide (CS_2) to produce xanthate ester groups in a process known as xanthation. Due to the limitation in the accessibility of CS_2 to some areas of the cellulose-caustic soda mix the material is not completely soluble at this time; instead a block copolymer of cellulose and cellulose xanthate is formed. The solution, which at this stage is a suspension, has a high viscosity and is therefore named “viscose”. The solution is allowed to stand and more completely react before being filter to remove materials which have not dissolved and the removal of any bubbles from the viscous solution. Fibers are formed in a process known as “wet-spinning” although similar reactions can be used to cast the regenerated cellulose material into films.^{22,23,24}

The wet-spinning process for viscose fibers forces the solution through a spinneret into a bath of sulfuric acid, sodium sulfate, and sometimes additional chemicals. The sulfuric acid reacts with the xanthate groups to form xanthic acid which releases the carbon disulfide and allows the cellulose hydroxyls to regenerate. The end result is filaments of regenerated cellulose. The newly formed filaments must be drawn in order to align the polymer chains and to control the final properties of the materials. The drawing of the filaments allows for physical properties, such as cross-sectional shape and area as well as modulus of elasticity to be finely controlled.^{22,24}

The lyocell process was developed in the 1980s and commercialized in the 1990s under the trade name “Tencel” by the Lenzing Inc. (Lenzing, Austria). The lyocell process is similar to the viscose process of rayon but utilizes fewer chemicals and may be conducted in a closed-loop system reducing the impact on the environment. In the lyocell process, cellulose is dissolved via an *N*-methylmorpholine-oxide system, instead of sodium hydroxide. This solvent may be filtered and reused throughout the process. The dissolved cellulose solution is forced through a spinneret in a similar manner to the viscose process; however the bath is a solution of acetonitrile or deionized water. The final properties of the regenerated fibers can be controlled in a similar manner to viscose. Spinneret design and tension in the bath can control the cross-sectional shape and area as well as the modulus of elasticity and even the optical properties of the fiber.^{22,25}

There are several major advantages of the lyocell method over the viscose process. The lyocell method utilizes a reusable solvent and allows for the process to be performed in a closed-loop. This allows the process to have a reduced impact on the environment. Eliminating the need for a sulfuric acid bath also reduces the impact on the environment. For the consumer, a significant advantage of the lyocell method is that the resultant material is easier to care for and has a better “hand” or feel against the skin. It is important to understand that the viscose process works by dissolving a cellulose derivative, xanthate, while the lyocell method directly dissolves the pure cellulose.²⁶ The more direct process of the lyocell method and reduction in chemical usage make it an ideal candidate for working with polymer/clay nanocomposite systems.

2.2 Review of Polymer/Clay Nanocomposites

Polymer/clay nanocomposites are an emerging field. Toyota’s Central Research and Development Laboratories began working on polymer/clay nanocomposites in the 1980s. Toyota was successful in developing a nylon-6/clay nanocomposite.^{2, 27, 28} The clay used for these early nanocomposites was the smectite clay, montmorillonite. Polymer/clay

nanocomposites show large changes in properties with small additions of clay nanoparticles. The large effect of a small addition of nanoparticulate reinforcement is due to the large surface area provided by the nanoparticles.

2.2.1 Nanocomposite Formation

Polymer/clay nanocomposites can be formed through four main processes. The four main processes are exfoliation-adsorption, *in situ* intercalative polymerization, melt intercalation, and template synthesis.²⁹

Exfoliation-adsorption requires that the clay be exfoliated in a solvent in which the polymer is soluble. Exfoliation is the process of swelling the silicate layers of the clay in order to allow the polymer matrix to interact with more surface area of the clay. In exfoliation-adsorption the solvent in which the matrix will be dissolved is also where the clay is exfoliated.²⁹

In situ intercalative polymerization makes use of a monomer to swell the silicate layers. The monomer, which will become the polymer matrix, performs the exfoliation and intercalation of the silicate layers. The monomer is then polymerized into the matrix polymer.^{30, 31}

Melt intercalation introduces the clay particles to the matrix polymer while the polymer is in the high energy molten state. Melt intercalation is only viable for thermoplastic polymers, since the polymer must be in a molten state.

The final process for the formation of polymer/clay nanocomposites is template synthesis. Template synthesis is the process of forming the silicate *in situ*. Organic templates are often used to synthesize inorganic materials. The precursor materials and template substrate can be used to control the properties of the synthesized material.³²

2.2.2 Polymers

Various polymers can be used for the matrix in a polymer/clay nanocomposite. The properties of the polymer are the major determining factor in selecting a nanocomposite

formation method. The initial work on polymer/clay nanocomposites was performed on nylon-6.^{2, 28} In the past 15 years many other polymers have been successfully used to create polymer/clay nanocomposites. These polymers include, but are not limited to, polyamides², polyimides³, methacrylates^{4, 5}, and polystyrene⁶. The diversity of polymers which can be used in polymer/clay nanocomposites is virtually unlimited.^{33,34,35,36,37} The vast majority of these polymers are thermoplastic.

Polymers can be divided into two classes, thermoplastics and thermosets. Thermoplastics can be repeatedly soften or melted when heated and then resolidified when cooled. Thermosets are unable to be melted or soften without irreversibly damaging the polymer. Thermoplastics have a melting point, T_m , which is higher than the polymer's degradation point, T_{deg} . Thermosets have the opposite characterization; they degrade before they soften or melt.

The melt intercalation process discussed previously takes advantage of the melting ability of thermoplastic polymers. Thermoset polymers must be dissolved before they may be processed into polymer/clay nanocomposites.

2.2.3 Cellulose

Cellulose is the polymer of interest in this research. Cellulose is a thermoset polymer. Previous research has been conducted on cellulose acetate and other derivatives of cellulose.^{16,17,18} These derivatives of cellulose are thermoplastics and may be manipulated via melt intercalation.

Cellulose is a large polysaccharide polymer with a high molecular weight. Cellulose is made up of a large number of hydrogen bonds which are individually weak but in large numbers impart great stability. These characteristics make cellulose difficult to dissolve. Section 2.1 addressed the current methods for dissolving cellulose and forming regenerated cellulose fibers.

Cotton fiber is the purest source of cellulose in natural existence. A cotton fiber is almost 100% cellulose, while wood and other sources of cellulose are closer to 50% cellulose.⁹ Current research is focusing on new ways to dissolve cellulose and address the difficulties of working with such a high molecular weight source of cellulose, such as cotton.³⁸

2.2.4 Clays

There are many possible types of clay for use in nanocomposites. Clays are made up of

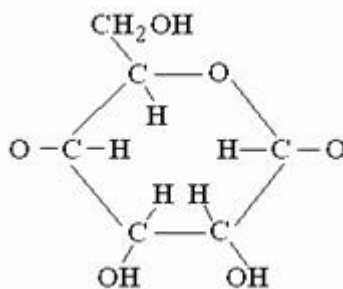


Figure 2.1 - Structure of Cellulose

silicate layers which must be separated to allow the polymer access to all of the interfacial regions. The process of separating the silicate layers is known as intercalation and exfoliation. The most heavily researched type of clay, for use in nanocomposites, has been smectite clays. Smectite clays are organic clays that can be swollen with small molecules. The basic structural unit of smectite clays is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. The layers are continuous in the plane of the clay sheet, but the bonds between sheets are weak and have excellent cleavage, allowing other molecules to enter between the layers causing intercalation and exfoliation. The most popular smectite clay for research has been montmorillonite; however kaolin and cloisite have been used successfully as well. There are also synthetic clays which can be used in place of natural clays.³⁹ Clays are chosen for a specific nanocomposite application based on their physical properties, such as aspect ratio and ability to be intercalated and exfoliated. The nanocomposite formation process,

as well as the desired end product, must be considered in selecting the appropriate nanoparticle clay.

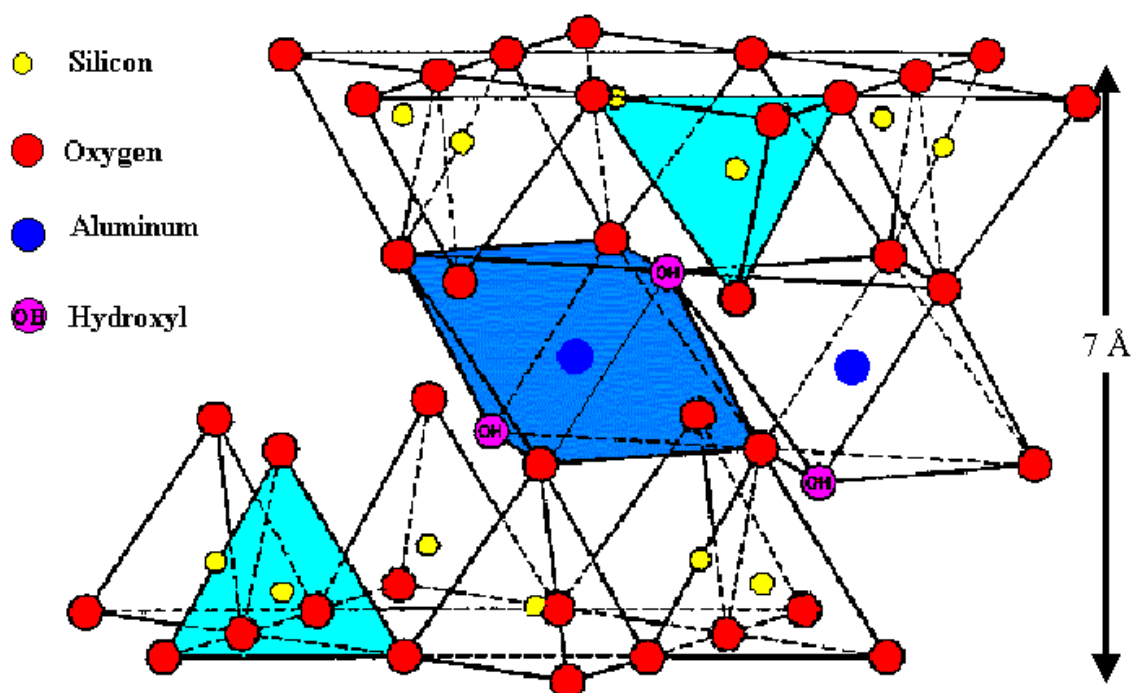


Figure 2.2 - Structure of Montmorillonite Clay⁴⁰

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Cellulose

Initial work was performed using cotton as the cellulose source. The cotton used was cotton linters and card waste obtained from the Cotton Structure and Quality Research Unit's Textile Pilot Plant at the Southern Regional Research Center (SRRC) in New Orleans, Louisiana. Cotton linters are short pieces of cotton that are left attached to the cotton seed after cotton ginning. Cotton linters are considered to be a reduced value product and have limited uses in the textile industry. In many cases linters are considered a waste material and must be disposed of by the cotton gins. Card waste is a by-product of the carding process in the manufacturing of cotton yarns. Carding is a process of combing and aligning cotton fibers to allow for the formation of yarn. The carding process removes short fibers from the array of cotton fibers as these short fibers are detrimental to yarn quality. Short fibers were chosen for three reasons. The status of short fibers as waste or reduced-value material makes it desirable to find alternative uses for the material. The shorter fibers have an increased surface area to volume, compared to longer fibers, and should therefore be more readily accessible to the solvent. The status of short fibers as less-desirable material makes the material more readily available.

Later work involved the exploration of the use of various sources of cellulose for the creation of the nanocomposite. Diverse sources of cellulose were obtained from the Cotton Structure and Quality Research Unit and the Cotton Chemistry and Utilization Research Unit at SRRC as well as the Cotton Ginning Research Unit in Stoneville, Mississippi. Cellulose sources used in the trials, in addition to cotton, include cotton gin waste, kenaf, ramie, and wood pulp. These other sources of cellulose were used to illustrate the applicability of the methods to sources of cellulose other than cotton. Cotton, as discussed earlier, has a high molecular weight making it

more difficult to dissolve. The alternative sources of cellulose should be more accessible to the solvent. Cotton is virtually pure cellulose and could be expected to give the best results. Other sources of cellulose, such as those listed here, contain other components, primarily lignin and other connective tissue, in addition to cellulose.

3.1.2 Clay

The clays used for this research were smectite clays. The initial work was focused on montmorillonite clay having an average length of 2000Å and width of 10Å. Additional work was performed using cloisite clay. The montmorillonite and cloisite were obtained from Southern Clay Products, Inc. (Gonzalez, TX) in an untreated state. In addition to montmorillonite and cloisite, various clays were examined to determine what, if any, differences they would have on the nanocomposite.

3.1.3 Chemicals

Various chemicals were needed for the exfoliation of the clay, dissolution of cellulose, and reprecipitation of the nanocomposite. The chemicals needed for this work were obtained from Aldrich Chemical Co. (St. Louis, Missouri) and used without further purification. Chemicals used in this work include 4-Methylmorpholine *N*-oxide (MMNO), lithium chloride/dimethylacetamide solution (LiCl/DMAc), and acetonitrile. The MMNO and LiCl/DMAc are solvents used in the dissolution of cellulose.^{22,38} Acetonitrile is recommended by the literature as the best solution for reprecipitation of the cellulose fibers.²²

3.2 Methods

Three methods of nanocomposite production were attempted. Cotton Nanocomposites containing 0-15 % (by weight) of montmorillonite clay as reinforcement material were produced

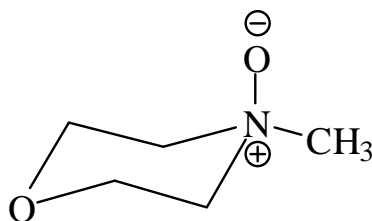


Figure 3.1 - Structure of 4-Methylmorpholine *N*-oxide

in batches of 1-2 grams of material. The cotton nanocomposites containing 0% reinforcement material were intended as control samples.

The first method was a simple method, intended to create a “one pot” formulation. The structure of the solvent is similar to intercalation agents often used to pre-treat montmorillonite clays (Figure 3.1).²⁹ It was hoped that the solvent could exfoliate the clay layers and then allow the cellulose polymer to intercalate with the silicate layers in the formation of the nanocomposite. The second method was a more traditional two-stage formulation. The last method utilized an alternative solvent for the dissolution of the cellulose. A range of approaches were tried in an attempt to identify the most practical and most effective approach to the creation of a cellulose/clay nanocomposite.

3.2.1 Method #1

Montmorillonite clay was exfoliated by rapid stirring in a 50% solution of 4-Methylmorpholine *N*-oxide (MMNO) in deionized (DI) water in a 500 mL three neck round bottom flask at ambient laboratory conditions. The solution became clear after one hour of stirring. Cotton was added to the flask after the solution became clear. The cotton/clay/MMNO solution was heated to reflux with continued rapid stirring. The cotton dissolved after 1-2 hours of stirring. The resulting solution was viscous and amber in color. The flask was immediately removed from heat, and the resulting material was reprecipitated into acetonitrile. The material was filtered and washed again in acetonitrile, followed by three washes in DI water. The samples were dried overnight at 120 °C under vacuum.

3.2.2 Method #2

Montmorillonite clay was pretreated with the ammonium salt of dodecylamine according to a previously published procedure.² The pretreated clay was then used in the following procedure. Pretreated montmorillonite clay was stirred rapidly in MMNO. After 30 min of stirring, cotton was added to the flask. The cotton/clay/MMNO solution was heated to reflux with continued rapid stirring. The cotton was dissolved approximately 1 hour after reaching reflux. The viscous amber colored solution was removed from heat and reprecipitated into acetonitrile. The material was filtered and washed a second time in acetonitrile. After filtration, the material was washed twice in DI water. After the final wash and filtration, the samples were collected and dried under vacuum at 120°C.

3.2.3 Method #3

Research has established that a lithium chloride/dimethylacetamide solution (LiCl/DMAc) could be used as a solvent for cellulose.⁴¹ DMAc is a traditional solvent used in the disassociation of montmorillonite clay after pretreatment with the ammonium salt of dodecylamine.² The third method was identical to the second method with the substitution of LiCl/DMAc for MMNO. This method failed to dissolve the cotton. Recent research indicates that with the high molecular weight of cellulose found in cotton more rigorous conditions are required with this solvent system before the dissolution of the cellulose can occur.³⁸

3.3 Sample Preparation

A film sample was made for each successful method of preparation. An aliquot of solution was removed from the flask of hot solution and pressed between glass slides to form the films. The slides were submerged in acetonitrile and soaked for 1 hour to remove the solvent. After removal from the acetonitrile bath, the slides were submerged in DI water and soaked. The top

glass slide was then removed, and the film was allowed to dry on the remaining piece of glass. A new razor blade, to prevent contamination, was used to remove the dried films from the glass.

Powder forms of the nanocomposites suitable for X-ray diffraction studies were produced by precipitation of the hot solution into acetonitrile. The precipitate was filtered and washed three times in DI water to remove residual acetonitrile. Blocks of the nanocomposites were formed by pouring the hot solution into a Petrie dish (Figure 3.2). The solution solidified into a cake-like form upon cooling. The nanocomposite blocks were dried under heat and vacuum then soaked in acetonitrile to attempt to remove any remaining solvent from the composite followed by re-drying under heat and vacuum.



Figure 3.2 - Photograph of a Cotton/Clay Nanocomposite Block in a Petrie Dish

4. TESTING TO DETERMINE PHYSICAL MAKEUP

4.1 Instrumentation

The physical composition and properties of the composite materials were tested in a variety of ways. X-ray diffraction (XRD) was performed by Dr. John Wiley at the University of New Orleans (New Orleans, Louisiana) to examine the crystalline structure of the composite materials. The goal of this testing was to examine the d-spacing of the silicate layers of the clay material to determine the amount of exfoliation and intercalation achieved. Transmission electron microscopy (TEM) was performed on the samples to visually examine the composition of the samples. TEM was performed at the University of Southern Mississippi (Hattiesburg, Mississippi) by Dr. Kenneth Mauritz.

Thermal analysis of the samples was conducted at the USDA-Southern Regional Research Center (New Orleans, Louisiana) utilizing both Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA was performed to measure the rate of mass loss with temperature change, the degradation temperature, and the percent char yield of the samples. TGA was conducted using a TA Instruments Hi-Res TGA 2950 (New Castle, Delaware). Samples were heated to 120 °C and held isothermally for one hour to normalize for moisture content. After air-cooling, scans were run from 40 °C to 600 °C at a heating rate of 10 °C/min. DSC was conducted to determine any changes in glass transition temperature or degradation point. DSC analyses were performed on a Mettler Toledo DSC 821 (Columbus, Ohio). Temperature scans were run from 30 °C to 300 °C at a heating rate of 5 °C/min.

4.2 Morphology

Methods #1 and #2 were successful in dissolving the cotton and being blended with the clay particles before being reprecipitated back into a solid material creating a true composite material. Method #3 was unsuccessful in dissolving the cotton and therefore no composite material was

created. The two successful methods produced a composite material, but it is not known from the act of creating the composite what type of composite material was created.

The first test to be performed was X-ray diffraction (XRD). The interspacing of the silicate sheets in the montmorillonite clay must be opened up to allow for the interaction of the cellulose with the clay. XRD shows diffraction peaks for the silicate layers when they are combined. Figure 4.1 shows the XRD patterns for a control sample made with 0% clay, a composite sample made with 15% montmorillonite via Method #2, and a sample of montmorillonite clay. The clay (c) demonstrates a peak around $9\ 2\theta$. This peak is due to the silicate layers. There is no peak for either the control or the composite material sample. No peak was expected for the control samples and the lack of a peak for the composite material demonstrates that the composite is a true nanocomposite with the polymer completely intercalated with the exfoliated clay nanoparticles. The samples from Method #1 retained a peak, indicating that the samples were not likely to be true nanocomposites, but microcomposites. The model put forth by Alexandre and Dubois²⁹ allows for the materials to be classified. This model is also illustrated in Figure 1.2. The lack of evidence for the exfoliation of the silicate layers in composites produced by Method #1 strongly suggests that microcomposite was formed. The pretreated clays of Method #2 appear to be exfoliated and thus a true nanocomposite.

XRD indicated that the composite materials produced by Method #2 were true nanocomposites. TEM was performed to visually confirm the level of intercalation. A control sample of regenerated cotton was examined to provide a baseline to compare the samples against (Figure 4.2). Figure 4.3 shows a photomicrograph of a cotton/clay composite composed of 7% montmorillonite clay. The large cellulose particles that are clearly visible in Figure 4.2 are almost completely obscured by the small nanoparticles of clay. This is a clear indication of the level of intercalation and exfoliation that was accomplished via Method #2.

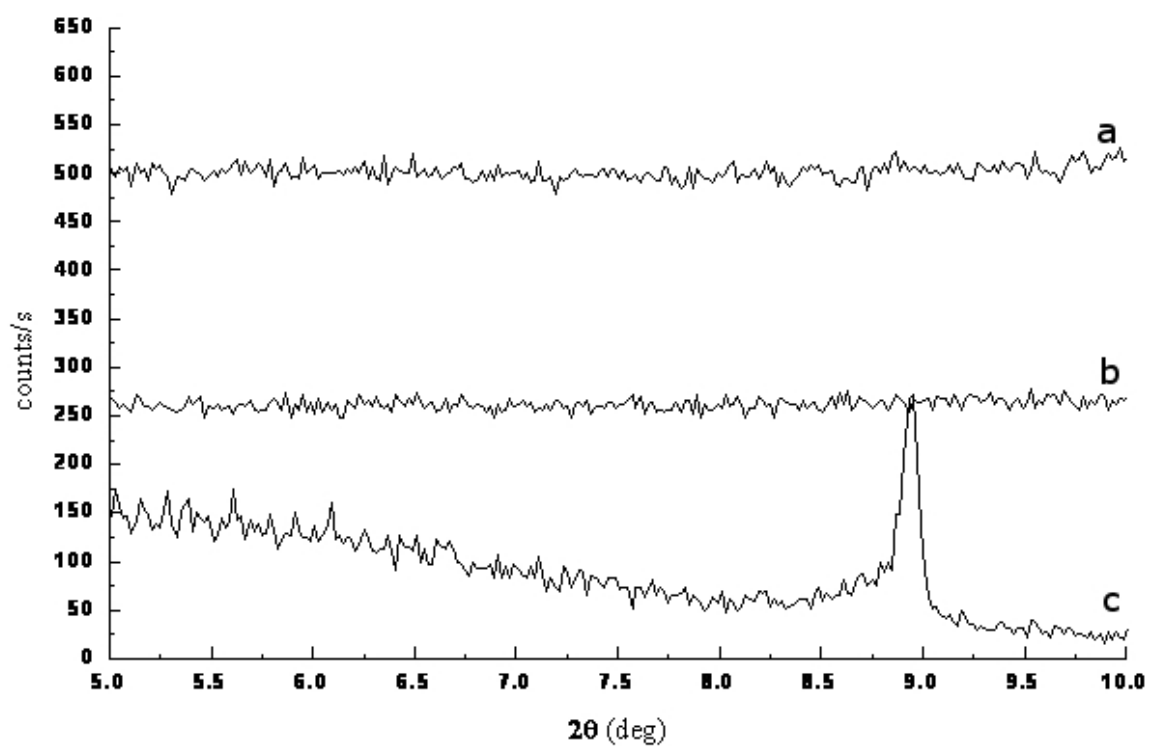


Figure 4.1 - XRD Patterns of (a) Control Cotton Sample, (b) Nanocomposite with 15% Montmorillonite Filler, and (c) Montmorillonite Clay

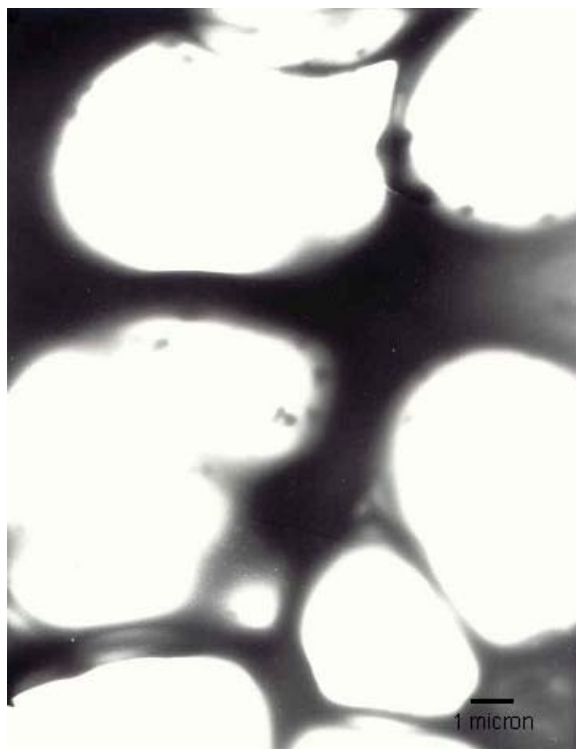


Figure 4.2 - TEM Photomicrograph of Regenerated Cotton Control Sample

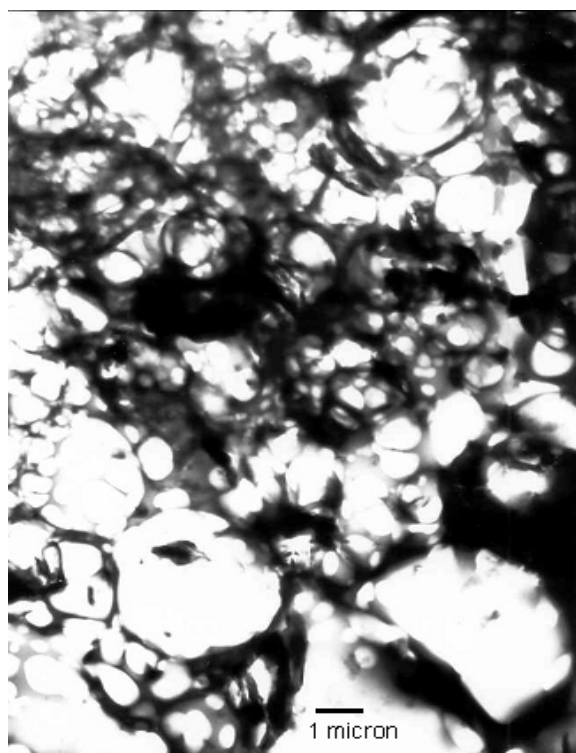


Figure 4.3 - TEM Photomicrograph of Cotton/Clay (7%) Nanocomposite Sample

4.3 Thermal Characterization

The DSC analyses did not show a glass transition temperature (T_g) below the onset of decomposition for any materials tested, including the control sample with 0% filler. This is a typical result for cotton. Cotton cellulose has a high degree of crystallinity and limited untethered amorphous content and therefore DSC thermograms rarely show a T_g . The nanocomposite material had a crystalline melt temperature (T_m) about 15° C lower than the control sample (186°C vs. 172°C) (Figure 4.4). The shift in T_m indicates that the nanocomposite has different thermal properties than the control material. It should be noted that the control cotton sample underwent dissolution in MMNO and likely consists of a mixture of cellulose II and cellulose III.⁹ There is the possibility that the addition of the clay particles has altered the crystalline structure of the cellulose. Verification of any changes to the crystalline structure would require more intensive crystallography work that is beyond the scope of this project.

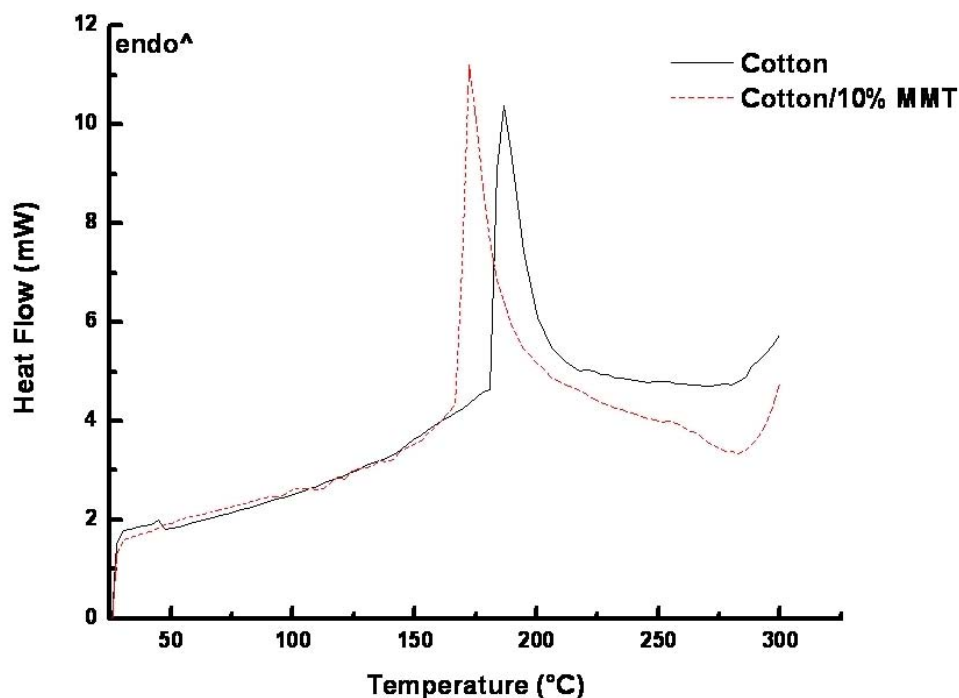


Figure 4.4 - DSC Thermograms of 0% and 10% Cotton/Clay Nanocomposite Sample

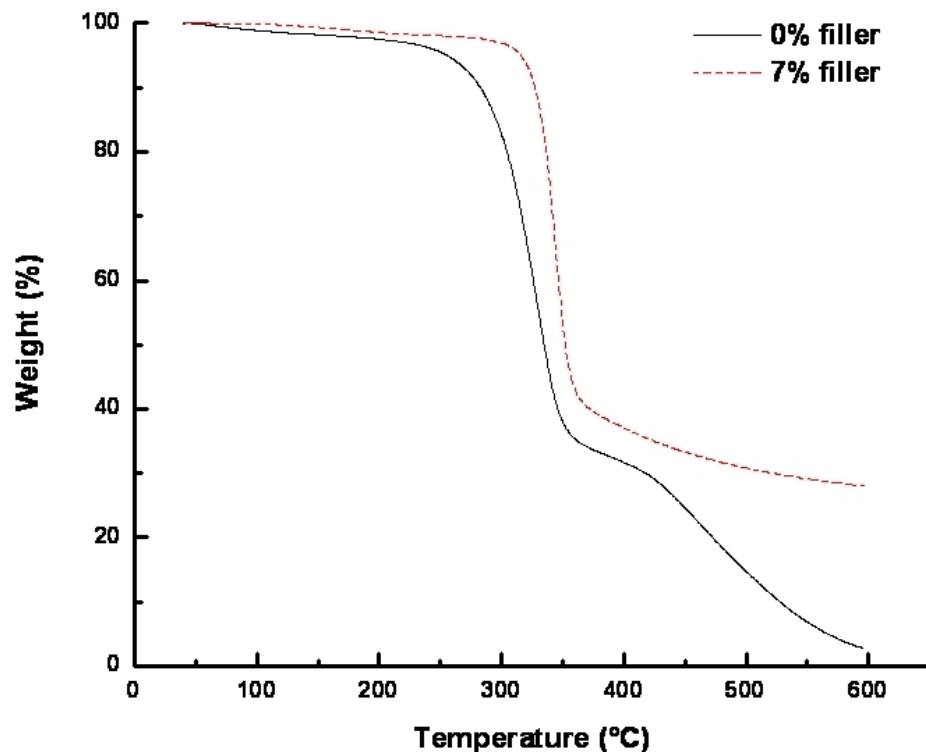


Figure 4.5 - TGA Thermograms Comparing Samples of 0% and 7% Clay Filler

The char yields of the composite material also differ significantly. Char yield is the percentage of material remaining from the original sample after the TGA run is complete. The char yield indicates the amount of the material which was not combustible or volatile at temperatures below 600°C. Table 4.1 lists the various char yields by percent clay filler. Materials containing only 1%, 2%, or 3% filler have relatively low char yields which are slightly increased above cotton without filler processed under similar conditions. The results at such low additive levels are not much different than raw cotton. The nanocomposites composed of 7%, 10%, and 15% clay additive show char yields around 30% of the initial weight of the original material. Figure 4.6 shows the TGA thermograms for these trials.

Table 4.1 – Char Yields of Nanocomposites

Weight % Clay	T _{dec} (°C)	Char Yield (%)
0	326	3
1	327	8
2	331	12
3	327	13
7	327	28
10	321	30
15	316	34

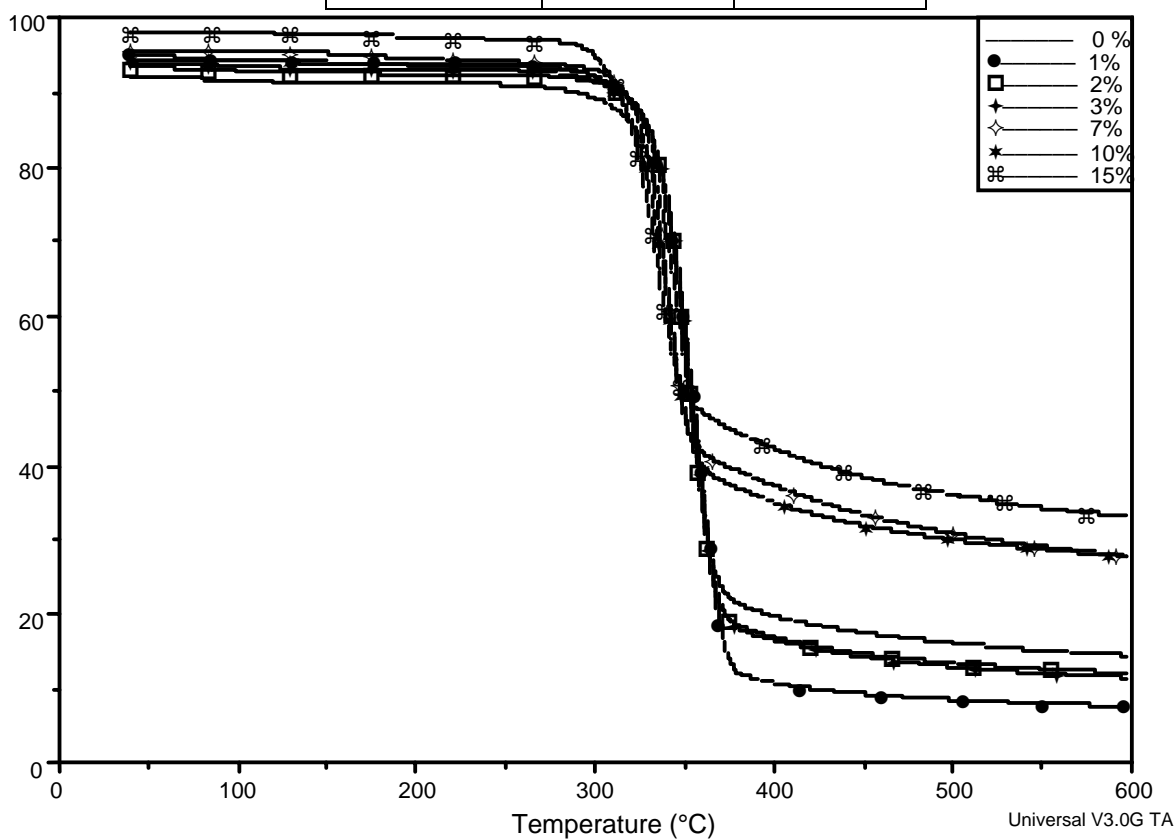


Figure 4.6 – TGA Thermograms for Various Clay Filler Amounts

4.4 Qualitative Analysis

As previously stated, films were made from each nanocomposite preparation. These films were opaque and brittle after drying. The films became transparent and pliable upon exposure to

the laboratory atmosphere. The powder and film forms of the nanocomposites did not exhibit any irregular behavior in the uptake of moisture from the atmosphere. The materials reacted in a manner that unprocessed cotton would be expected to react. The larger blocks of composite material, such as Figure 3.2, did exhibit increased water uptake from the environment. The excessive water uptake is most likely due to residual solvent in the material and could be alleviated with a more thorough processing of the material to ensure the complete removal of the hydroscopic MMNO solvent. In handling the films of the composite materials several observations were made. The films from Method #2 exhibited much more strength and were easier to handle than Method #1. The water uptake of samples from Method #1 appeared to be greater than Method #2. These observations, in conjunction with the XRD results, led to the abandonment of Method #1 and the focus on Method #2 for all other analyses, such as DSC, TGA, and TEM. The films produced by Method #2 felt and behaved, during handling, identically whether they were the control samples or the nanocomposite samples.

5. THERMAL PROPERTY CHANGES

5.1 Flammability

Combustion requires three components: 1) fuel, 2) oxygen, and 3) energy (heat). These three elements must be present for combustion to occur and are known as the “fire triangle”. Traditional flame retardants work by depriving the system of at least one of the three components. Fire extinguishing methods work in the same manner. A carbon dioxide fire extinguisher displaces the air at the point of combustion and therefore removes the oxygen from the triangle so combustion can not continue. Spraying water on a fire is a way to reduce the heat energy at the point of combustion and therefore combustion can not continue.

Certain flame retardant materials, such as Nomex[®], are members of the meta-aramid family of materials. These meta-aramids function by having a T_{dec} of around 400°C or higher depending on the specific makeup.⁴³ Materials which have such a high T_{dec} do not provide fuel to the combustion reaction, since the material is not degrading. The melting temperature, T_m , of these materials must be as high or higher than T_{dec} in order for the material to be useful at such elevated temperatures. If the material does not have physical integrity, then it is of limited use.

Mylar type materials can be used in flame retardant materials by reflecting some of the heat away from the material and thus reducing the temperature which the substrate material is exposed to. This is one of the few effective ways that a flame retardant material can remove the energy leg from the fire triangle.

The last method by which a flame retardant material can work is to remove the oxygen from the fire triangle. The way to remove oxygen from the fire triangle is to either displace it, like in a fire extinguisher, or to provide an impediment between the oxygen and the heat and fuel. This method is way in which most flame-retardant finishes work.

Some flame-retardant finishes on fabrics do work by raising the T_{dec} . Most successful finishes on materials such as cotton work by removing oxygen from the fire triangle. The way in which these materials work is counter-intuitive. The T_{dec} is lowered by the chemical finish allowing for the rapid formation of a char layer. Char is not readily combustible and provides a barrier for the oxygen and heat to get to the material beneath it.^{9, 15, 44} An unusual property of polymer/clay nanocomposites is that they do not always lower the T_{dec} of the original polymer while displaying an increase in flame retardance.

5.2 Mechanism

The mechanism by which polymer/clay nanocomposites effect reduced flammability in the original polymer is not clearly understood.⁴⁵ One finding is that the introduction of clay to the polymer allows for the formation of carbonaceous char in a nanocomposite whereas the original polymer would not form a char layer.⁴⁶ This mechanism does explain the increased flame-retardance shown in many polymer/clay nanocomposites. Gilman, et al. did discover a downside to this mechanism, however. The traditional use of ammonium salts to assist in the intercalation and exfoliation of montmorillonite clays may lead to the degradation of the montmorillonite in some instances.⁴⁶ An alternative method of pretreating the montmorillonite clay could resolve this issue.

Cellulose does naturally form a carbonaceous char during combustion. The results shown previously, such as Table 4.1, demonstrate that the addition of the montmorillonite did significantly increase the amount of char formed during combustion. The large amount of char formation is a good indicator that the cellulose/clay nanocomposite material will be flame retardant.

5.3 Diffusion

Formation of a substantial char layer is an indicator of flame resistance. The char does not readily burn, but this alone does not satisfactorily explain the flame retardance that is demonstrated by the polymer/clay nanocomposite. Polymer/clay nanocomposites are believed to function by creating a barrier layer within the material, in addition to the increased char layer on the surface of the material. The barrier layer prevents oxygen from diffusing through the material. Gas permeability tests have been performed on a number of polymer-clay nanocomposite systems.^{2,39,47,48,49,50} Permeability has been measured of H₂, He, and O₂ gases. The testing for gas permeability measures the resistance of the sample to diffusion of the gas through the sample.

The nanoparticles are able to fill voids in the polymer matrix, as demonstrated by Figures 4.2 and 4.3. The small size and large aspect ratio of the nanoparticles of clay create a torturous route through the matrix for the gases to pass. Figure 5.1 illustrates a concept proposed by Yano to explain decreases diffusivity of gases through polymer/clay nanocomposites.² The total path of diffusion through the nanocomposites can be described by Equation 5.1.

$$d' = d + d \cdot L \cdot V_f / 2W \quad (5.1)$$

d' : total path of diffusion

d : thickness of the nanocomposite

L : average length of a clay particle

W : average width of a clay particle

V_f : volume fraction of clay particles in the nanocomposite

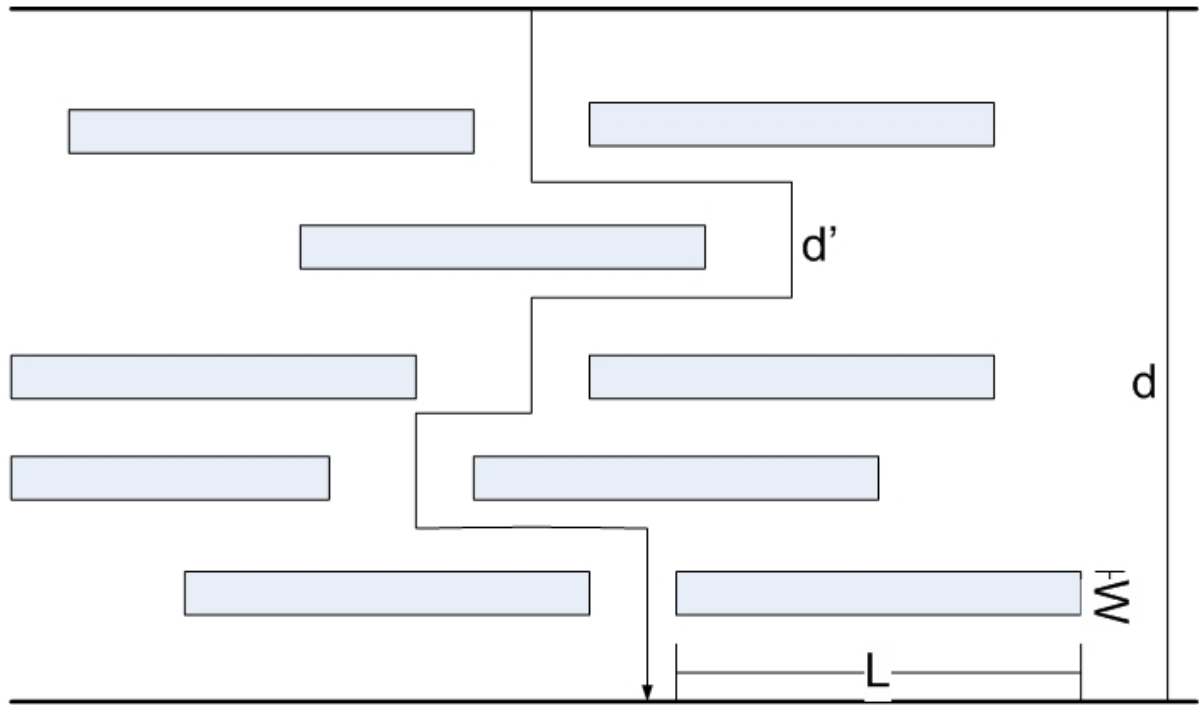


Figure 5.1 Model for Gas Diffusion through Polymer/Clay Nanocomposites

The materials science term “tortuosity factor” also comes into play in understanding the relationships at work. Tortuosity factor (τ) is the distance a molecule must travel to get through a film in relation to the thickness of the film. The nanocomposite barrier layer can be modeled as a film for this application, resulting in Equation 5.2, which can be resolved into Equation 5.3

$$\tau = d' / d \quad (5.2)$$

$$\tau = 1 + L \cdot V_f / 2W \quad (5.3)$$

The permeability of a polymer nanocomposite to a gas is described as a permeability coefficient, similar to a diffusion coefficient. The permeability coefficient (P_c) can be calculated from Equation 5.4.

$$P_c = P_p / \tau \quad (5.4)$$

P_p : permeability coefficient of matrix polymer

Research has shown that as little as 2 wt% addition of clay can decrease gas permeability coefficients by 50%.² Additionally, the permeability of water vapor was decreased ten fold.⁴⁸ The magnitude of decrease in permeability varies depending upon the properties of the polymer and the clay.

Clays such as synthetic mica and montmorillonite yield highly exfoliated nanocomposites. Other clays, such as saponite and hectorite, retain a degree of intercalation. The intercalated nanocomposites show vastly superior performance for resistance to gas diffusion compared to the pristine polymer materials, however they are several-fold less effective than the completely exfoliated samples.⁴⁸ It is unclear if the magnitude of difference is caused by the intercalation or the differences in aspect ratio. (Table 5.1)

Table 5.1 – Representative Clays and Their Aspect Ratio

Clay	Aspect Ratio
Hectorite	50
Saponite	170
Montmorillonite	200
Synthetic Mica	1230

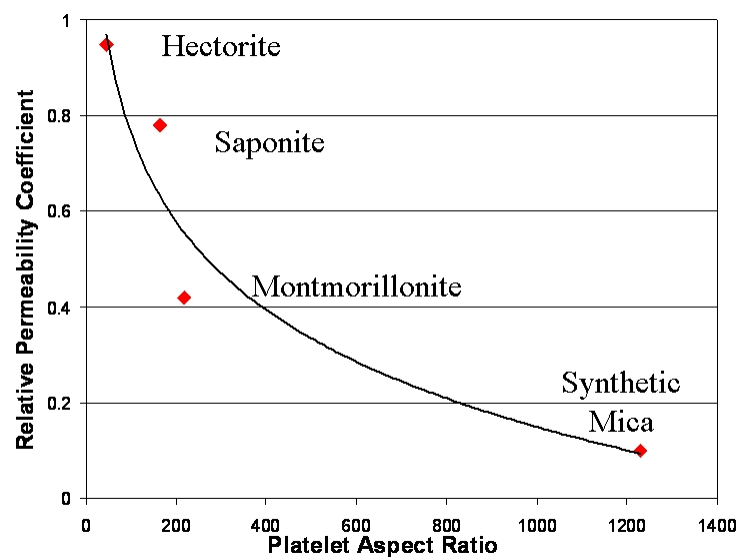


Figure 5.2 - Effect of Platelet Aspect Ratio

6. MECHANICAL PROPERTY CHANGES

6.1 Tensile Strength Testing

One goal of the research was to produce a fiber based on cellulose, which could compete with synthetic fibers in textile applications. The tensile strength of textile fibers is important as the strength of a textile fiber is a major factor in determining the end strength of a spun yarn. Spun yarns are composed of a bundle of individual fibers that have been twisted together. Regenerated cellulosic fibers may be used in either a fiber or filament state. Filaments are long continuous extrusions of material in an equivalent diameter to either single fibers or finished yarns. Filaments which are a diameter equivalent to a finished yarn are generally referred to as monofilaments. Finer filaments will be used in an assembly with other fine filaments to achieve desired strength and performance where a monofilament will be used individually.

The fibers produced by this work are coarser than a traditional textile fiber and may be more akin to a monofilament. Detailed information on the fiber production is given in Chapter 7. The dimensions of the fiber play a role in choosing the appropriate tensile testing method. Cotton fibers may be tested for strength by a variety of methods and instruments. The most common method to test the strength of a bundle of cotton fibers is through the use of a High Volume Instrument (Uster Corporation, Knoxville, TN).⁵¹ Single textile fibers may be tested using a variety of methods. The most common method for testing a broad range of individual textile fibers is ASTM D3822⁵², which was employed for this work. An Instron (Norwood, MA) Model 5567 Universal Materials Testing Machine was utilized for this testing. The fibers were mounted individually in a jaw apparatus designed to test single fibers and filaments on constant-rate of extension (CRE) style tensile testing machine. A gage length of 25.4 mm was used with a rate of extension of 15 mm/min.

6.2 Tensile Strength Results

Fibers were produced from the nanocomposite process with 0% and 7% montmorillonite clay additive. The fibers were initially very dry and brittle; however, the fibers rapidly absorbed moisture from the air and became more flexible. The fineness of individual cotton fibers made it impossible to compare the significantly coarser nanocomposite fibers directly to cotton. The 0% additive samples were treated as a control to measure the effect of adding clay nanoparticles to the cellulose. The 7% clay additive level was chosen for this test as it has shown to be an optimum amount of clay for thermal enhancement of the cellulose polymer based on TGA results.

Representative results of the tensile testing are shown in Figure 6.1. The control specimen demonstrates a smooth curve and constant modulus until the ultimate stress is reached at 6.98 MPa with no yield point before breaking. The 7% clay nanocomposite has an ultimate stress of 12.5 MPa. The force-elongation curve for the 7% clay sample is not as smooth and uniform as the control specimen. The 7% clay sample exhibits a higher initial modulus with a yield stress approximately less than half of the control sample. However, the clay additive sample has a ultimate stress approximately 80% greater than the control specimen.

The clay additive increases the overall strength of the regenerated cellulose structure and significantly alters the modulus of elasticity. The clay additive increases the ductility of the regenerated cellulose. The addition of particulate reinforcement to composite materials is known to increase ductility and improve resistance to impact forces.¹

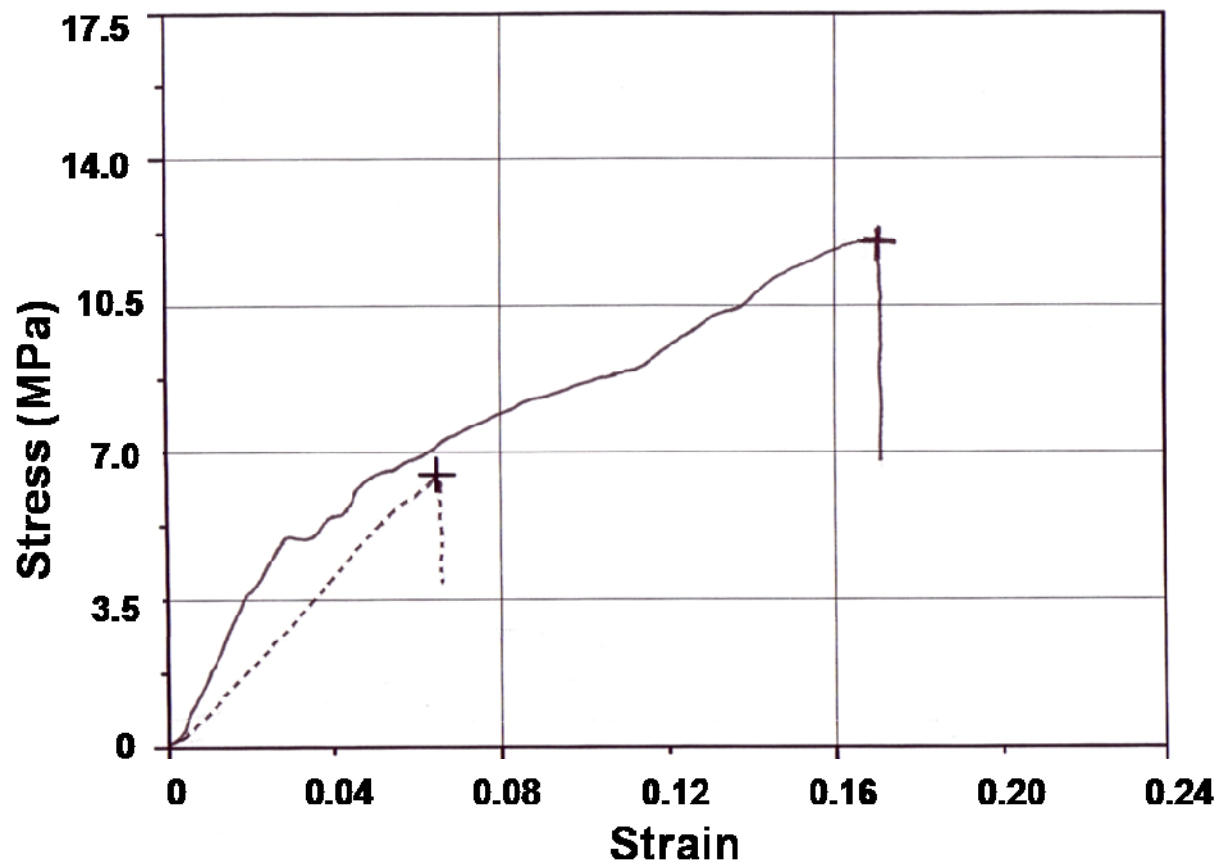


Figure 6.1 Tensile Testing Results of Nanocomposite Fibers
(dashed line is 0% clay, solid line is 7% clay)

7. MATERIAL PRODUCTION

7.1 Fiber Production

Cotton fiber was used as the cellulose source for this research. The goal is to produce a cellulose based composite material with enhanced flame retardance. Textile applications usually require materials in fiber form. The nanocomposite was initially produced as small films, blocks and powders. The high molecular weight of cotton cellulose causes the polymer to naturally attempt to form long chains and a fiber form is a natural outcome of this tendency.

The manufacture of regenerated cellulose fibers has been well documented for the viscose and lyocell methods.^{22,24} A typical industrial dry-jet wet fiber spinning process for regenerated cellulosic materials is shown in Figure 7.1.

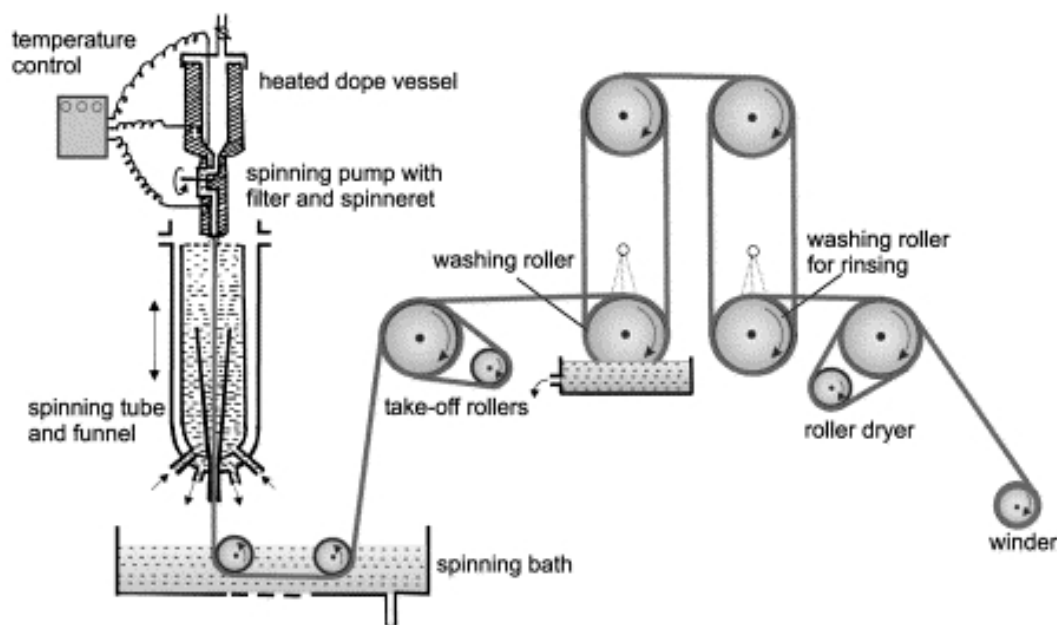


Figure 7.1 - Schematic of the Dry-Jet Wet Fiber Spinning Process²²

The industrial process was mimicked for the production of fibers on a laboratory-scale. The work of Broughton⁵³ showed that a syringe or HPLC pump could be modified to produce uniform and consistent fibers. The micro-scale spinning system for this work consisted of an

automated syringe pump (Model 210, KD Scientific, New Hope, Pennsylvania) with a syringe pump and needle as the spinning tube and spinneret, as shown in Figure 7.2. The method was attempted using a handheld syringe to verify the concept before adapting a syringe pump. The spinning bath for this prototype was a catch pan filled with the reprecipitation solvent (Figure 7.3). Initial trials, reported in 3.2 utilized acetonitrile as the reprecipitation solvent. Additional work was performed and demonstrated that the acetonitrile could be replaced with DI water if multiple rinses were used to provide a clean and fresh DI water bath. The micro-scale system was sufficient to produce approximately 25 grams of fiber per batch. The needle gauge could be varied to produce different diameter fibers, however smaller gauge needles resulted in higher pressures being needed to extrude the fiber and the syringe pump could be stalled. An 18 gauge needle was found to be ideal for the production of textile fibers. An 18 gauge needle has a nominal outside diameter of 0.05 ± 0.0005 inches, with a nominal inside diameter of 0.033 ± 0.0015 inches. The 18 gauge needle produced fibers with a nominal diameter of 0.033 inches or approximately 840 μm . A single cotton fiber is on the order of 12-20 μm .¹² Synthetic fibers are often much coarser than single cotton fibers. It is believed that the nanocomposite could be produced in smaller diameters on a commercial production unit.

The fibers produced using the micro-scale system were brittle, although they did become flexible as some moisture was absorbed from the atmosphere. Overall, the fibers appeared to be more brittle than traditional textile fibers, however it is believed that this could be controlled in a larger-scale production environment since both the control and the nanocomposite fibers exhibited the same characteristics.

7.2 Nonwoven Production

7.2.1 Introduction to Nonwovens

Textile fabrics can be generally classified into three categories, wovens, knits, and nonwovens. Woven and knit fabrics are made from yarns which were produced by processing fibers through a variety of processing steps including carding, drawing, and spinning. Nonwoven textiles are a field that has been largely dominated by the synthetic fiber industry. Nonwoven fabrics are not woven, as the name suggests, nor are they knit. Nonwoven fabrics are



Figure 7.2 – Micro-scale Fiber Spinning System

constructed from a random or semi-random assembly of fibers which are held together through various fiber consolidation techniques, such as fiber entanglement or melt-bonding of the fibers. Perhaps the best known example of a nonwoven material is paper, however nonwoven fabrics have found applications in a myriad of industries. Nonwoven fabrics can be found in furniture, bedding, sanitary products, erosion control materials, and wipes.

The most common consolidation techniques are hydro-entanglement, needle-punching, melt-bonding and spun-lacing. Hydro-entanglement and needle-punching hold the material together by entangling the fibers. The entanglement of fibers is accomplished using high-pressure jets of



Figure 7.3 – Extrusion of Fiber into Reprecipitation Solvent

water for hydro-entanglement and is most common in medical applications as the water jets provide another level of cleaning. Needle-punching accomplishes the fiber entanglement by passing webs of fibers through beds of barbed needles which repeatedly punch in and out of the fabric, entangling the fibers as the web passes through the machine. Fiber entanglement methods can work with any type of textile fiber.

Melt-bonding and spun-lacing hold materials together by fusing the fibers together. In the melt-bonding process a web of fibers is passed through a set of heated rollers. The heated rollers cause the fibers to partially melt, thereby fusing together when cooled. The spun-lacing

technique lays a continuous stream of melted polymer onto a moving conveyor belt while moving in a random pattern. The polymer stream is cooled and becomes a continuous material that has the appearance of entangled fibers. Melt-bonding and spun-lacing require the raw materials to be thermoplastics. In the case of melt-bonding, the entire web of fiber does not need to be a thermoplastic polymer, but a substantial enough portion of the web must be in order to sufficiently bond the thermoset polymers into the final material.

Cotton dominates the traditional textile market for apparel. As discussed earlier, a flame retardant cotton-based fiber would allow cotton to compete with synthetic fibers in applications that cotton currently is not suitable for. The same can be said of the nonwovens industry. The nonwoven production techniques led themselves to longer fibers and fibers which can be engineered to perform as needed. Regenerated cellulosic fibers, such as the cotton/clay nanocomposite fibers may be able to compete with synthetic fibers in the nonwovens market. Work was undertaken to produce some sample nonwoven materials to determine the feasibility of the nanocomposite fibers use in nonwovens. It was also thought that nonwovens would be a way to produce a tangible material from the nanocomposite fibers produced in 7.1

7.2.2 Manufacture of Nonwovens

The nonwoven material that could most readily be made with cotton/clay nanocomposites produced on a laboratory scale was a type of paper. The nonwovens research facility at SRRC in New Orleans, Louisiana contained a laboratory-scale Voith (Heidenheim, Germany) paper making facility. The laboratory-scale papermaking facility contains a “sheet mold” for the creation of a loose sheet from pulp slurry, a press for removing large amounts of liquid and consolidating the fiber array, and a steam plate for drying the final product (Figure 7.4).

Cotton/clay nanocomposite fibers were produced on the micro-scale fiber spinning system from 7.1. A step-by-step demonstration of the process is reported in Appendix A. These fibers were placed into a Waring (Torrington, Connecticut) blender with a liter of DI water. The fiber/water solution was blended on high speed for approximately 30 seconds until a fiber and water slurry was created. A layer of cotton gauze or cheese-cloth was placed on the bottom of the sheet mold (Figure 7.4 a) to assist in handling the fiber mat before it was fully formed. The liquid chamber of the sheet mold was then lowered and latched in place to create a water tight

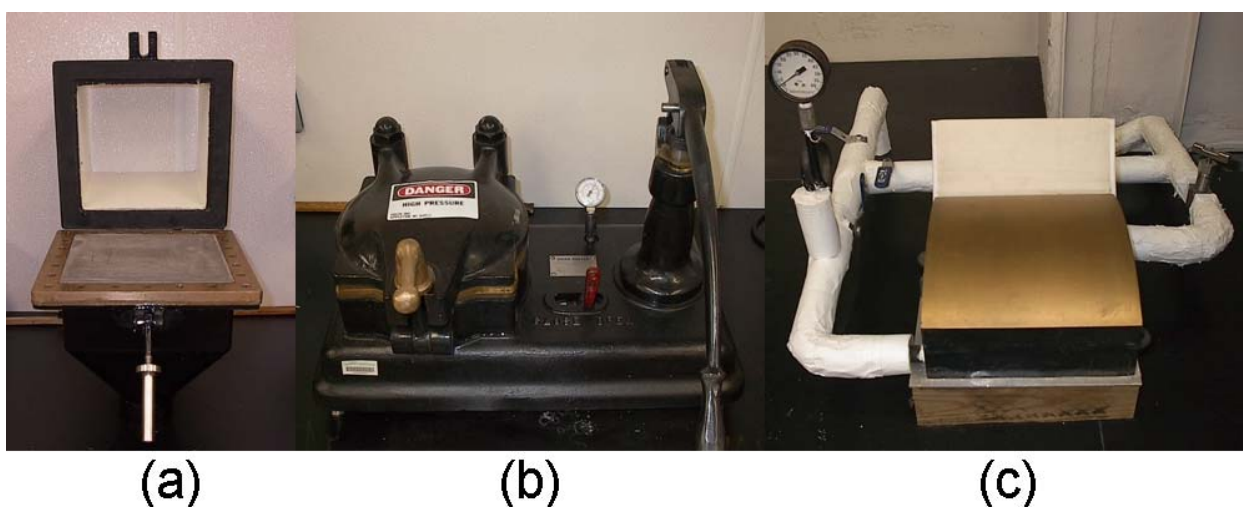


Figure 7.4 – Laboratory-Scale Papermaking, (a) Sheet Mold, (b) Press, and (c) Steam Plate

seal. A series of valves on the sheet mold were opened to partially fill the sheet mold with water before receiving the slurry. The slurry was poured into the sheet mold on top of the gauze layer. The slurry was gently stirred to ensure a uniform and random distribution of the fibers. The water from the slurry was drained from the sheet mold when the solution appeared to be uniform and containing no clumps. After draining, the newly formed sheet of fibers was removed from the sheet mold by lifting the gauze substrate. The sheet was transferred to a hydraulic press (Figure 7.4 b) to be pressed in order to remove excess liquid and consolidate the fibers into a more solid mass. The final step in the process involves transferring the pressed sheet to the steam plate (Figure 7.4 c). The steam plate is a brass plate which is heated via steam coils. The

freshly pressed sheet of fibers is placed on the plate and the gauze substrate is removed. A weighted canvas sheet is placed over the fiber sheet to apply pressure to the nonwoven as it is dried. The fiber sheet is removed from the steam plate when it is dry and the nonwoven is formed (Figure 7.5).

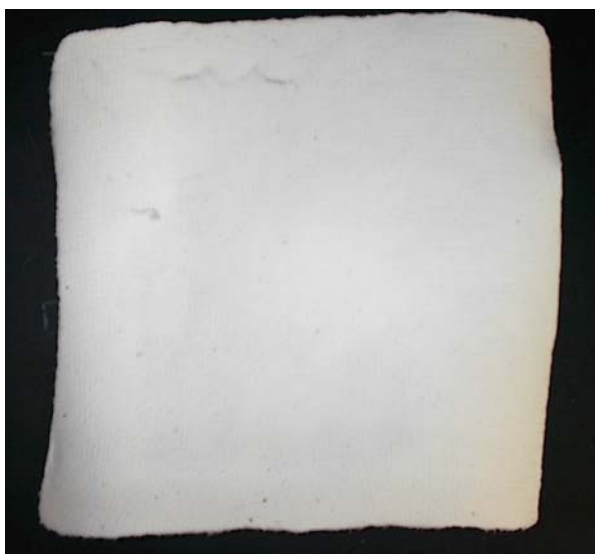


Figure 7.5 – Nanocomposite Nonwoven

7.3 Alternative Sources of Cellulose

The method put forth in 3.2.2 was shown to create cellulose/clay nanocomposites from cotton. The method was believed to be valid for all sources of cellulose; however this had not been proven. A program was begun to test alternative sources of cellulose and an additional type of clay to ensure that the cellulose/clay nanocomposite preparation method was versatile and applicable to other clays and sources of cellulose.

Ramie and kenaf fibers were obtained from the Mini-Spinning Laboratory at SRRC. Wood pulp samples were obtained from the Cotton Chemistry and Utilization research unit at SRRC. Ramie and kenaf are bast fibers, as opposed to cotton which is a seed fiber. Ramie is a strong fiber with application in textiles, rope, and some specialty gaskets. Kenaf is a fast growing plant used primarily as feed stock for lower quality paper, such as newsprint. Bast fibers are harvested

from the inner bark, or bast, of certain plants. Bast fibers are longer than seed fibers and have higher lignin content. Wood pulp is a processed wood product used to make paper. Wood pulp generally comes from softwood trees such as spruce, pine and fir; however wood pulp may be produced from hardwood trees as well. The wood pulp used for these trials was made from pine.

Cloisite clay was chosen to be incorporated into the nanocomposites as an alternative to montmorillonite. Cloisite is an organic clay which is a modified form of montmorillonite. Trials were run utilizing 7 wt% of clay additive for each nanocomposite. The weight percent of clay was chosen based on previous results in 4.3.

Cellulose/clay nanocomposites were produced using Method #2 from 3.2.2. The samples were subjected to both TGA and TEM analysis. TGA results (Table 7.1) show that both montmorillonite and cloisite alter the T_{dec} of the nanocomposite. T_{dec} is higher for both types of clay than in the control samples of regenerated cellulose with no filler. The char yields are significantly higher for both clay types than the control samples for all sources of cellulose. TEM analyses demonstrated that the clay nanoparticles were thoroughly distributed throughout the polymer matrix, regardless of clay or polymer type. TEM photomicrographs for the cloisite nanocomposites are shown in Figure 7.6.

Table 7.1 – TGA Results for Various Cellulose/Clay Nanocomposites

Sample		T_{dec} (°C)	Char Yield (wt%)
Cotton	Control	282	3
	Montmorillonite	327	28
	Cloisite	311	23
Ramie	Control	290	16
	Montmorillonite	335	32
	Cloisite	313	27
Kenaf	Control	283	12
	Montmorillonite	321	25
	Cloisite	305	22
Wood Pulp	Control	284	13
	Montmorillonite	313	25
	Cloisite	300	21

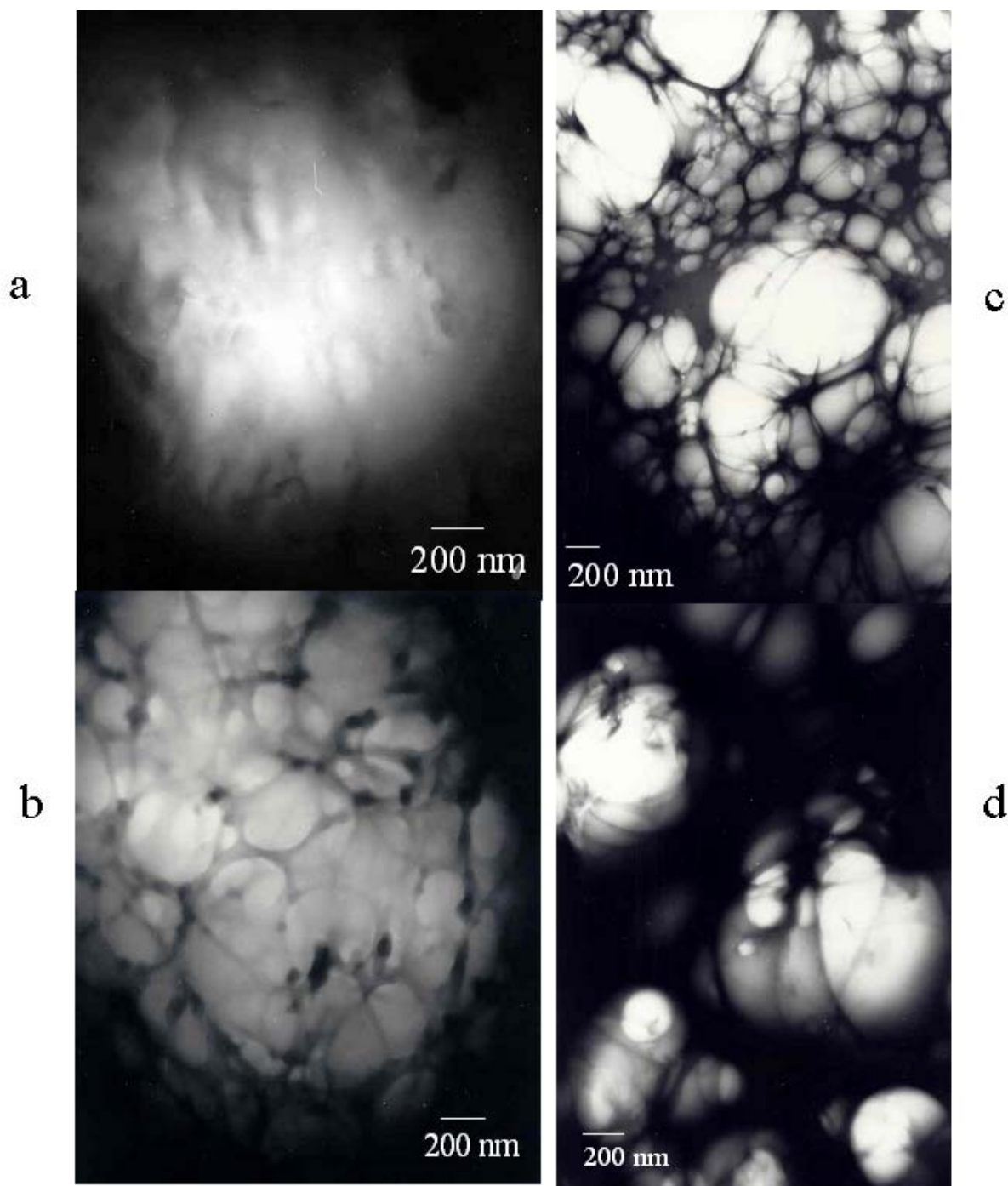


Figure 7.6 – TEM Photomicrographs of Cloisite Nanocomposites: (a) Cotton, (b) Kenaf, (c) Ramie, and (d) Wood Pulp

8. SUMMARY, CONCLUSIONS, AND FUTURE PLANS

8.1 Summary

A new type of polymer/clay nanocomposite was produced using cellulose as the polymer matrix. A method was developed to allow cellulose to be used as the polymer matrix in polymer/clay nanocomposites. Physical analysis of the samples, including X-ray diffraction and transmission electron microscopy, has validated the creation of a true nanocomposite material with complete intercalation and exfoliation of the silicate layers. The nanocomposite material displays enhanced thermal properties which indicate some degree of improved flame resistance from the original polymer. The polymer/clay nanocomposite system makes use of the existing lyocell method for producing regenerated cellulosic fibers.

Studies confirmed that the method utilizing pretreatment of the clay using ammonium salt of dodecylamine before dissolution of cellulose in a heated solution with MMNO and the clay additive created a viscous solution which could be reprecipitated as a nanocomposite of cellulose and clay. Attempts to utilize the MMNO solvent to exfoliate the clay particles and create a “one-pot formulation” created microcomposites, but was unsuccessful at forming true exfoliated nanocomposites. Acetonitrile is the standard reprecipitation solvent, however work was performed which demonstrated that DI water could be used in sufficient quantities to replace the acetonitrile.

A micro-scale system to produce textile quality fibers from the nanocomposite solution was developed. Cellulose/clay nanocomposite fibers were produced and proved to be stable and able to withstand the rigors of textile processing. A nonwoven material was produced utilizing laboratory-scale paper processing equipment. This nonwoven material validated that the nanocomposite material could be converted into traditional textile products.

Initial work was conducted on cellulose obtained from cotton fiber. This initial work allowed for some experimentation with new solvent systems for the dissolution of cotton cellulose. Additional sources of cellulose were tested with the developed method to determine the applicability to alternative sources of cellulose. The alternative sources of cellulose were chosen to represent a broad cross-section of natural sources of cellulose, such as vegetable plant matter (bast fibers) and low-cost, high-lignin content sources such as trees (wood pulp). The method of nanocomposite preparation developed by this work was found to be applicable to a variety of sources of cellulose.

The initial work utilizing montmorillonite clay was successful. A second type of clay, cloisite, was tested and found to produce acceptable results in the nanocomposite. The developed method has been proven to be robust and versatile for use with a variety of sources of either cellulose or clay. All clay and cellulose sources utilized in these trials showed improved thermal properties using the developed method to create cellulose/clay nanocomposites.

8.2 Conclusions

A polymer/clay nanocomposite was developed from cellulose for the first time. The physical makeup of this nanocomposite was examined via a variety of techniques to ensure that the material is a true nanocomposite. The thermal characteristics of the nanocomposite material were analyzed by both thermogravimetric analysis and differential scanning calorimetry. The nanocomposites were produced as films, blocks, powders, and fibers. Preliminary testing of the effect of the nanofiller on the strength of the polymer matrix was performed. A unique small scale fiber production system was created to support this research. Fibers produced via the small-scale production system were converted into nonwoven materials to determine if the fibers could withstand traditional textile processing.

Polymer/clay nanocomposites provide enhanced thermal properties, such as flame retardance, to the original polymer matrix material. The polymer/clay nanocomposites require only small additions of reinforcement material in comparison to traditional composite materials. The research reported found that as little as 1 wt% of clay nanoparticles effected a change in the thermal properties of the original cellulose. The ideal additive amount appears to be around 7 wt% of clay to the cellulose matrix for optimal char yield.

Montmorillonite clay and cloisite clay are both effective clays at creating a cellulose/clay nanocomposite. Montmorillonite and cloisite are both effective at creating an increase in char yield. The montmorillonite appears to be slightly more effective then cloisite, however optimum char yield to effect a change in flame retardance was not determined.

The mechanism of flame retardance in polymer/clay nanocomposites is not clearly understood. However, a possible explanation for the flame retardant properties exhibited by polymer/clay Nanocomposites was found in this research. Theoretical and experimental work was performed to determine the influence of nanoparticle size on the permeability of the nanocomposites. The permeability and associated diffusivity of the nanocomposites has been shown to aid in the formation of a boundary layer of char. This boundary layer is known to inhibit the combustion of the base material.

Cellulose/clay nanocomposites offer a durable flame retardant mechanism that can not be altered by abrasion or laundering due to the clay particles being distributed throughout the polymer matrix. The barrier properties of the nanocomposite, in conjunction with the durability of the finish, should allow cellulose based fibers to compete in areas which have been previously inaccessible to natural fibers. The development of new materials based on the cellulose/clay

nanocomposite has the potential to aid the \$27 Billion cotton industry in competing with synthetic fibers.

The developed method represents an economically viable approach to producing flame retardant textile materials. The work has shown that a variety of source of cellulose successfully works as the feedstock for the polymer matrix; this allows the manufacturer to use the most cost-efficient source of cellulose as market prices fluctuate. The nanoclay filler materials are inexpensive and readily available. The developed process utilizes an existing commercial process which would require very little modification to produce the nanocomposite materials.

8.3 Future Plans

The reported research has been patented and rights assigned to the United States Department of Agriculture (Appendix B).⁵⁴ Commercial interest in the cellulose/clay nanocomposite has been very active. The scale up of the developed method to industrial-scale would need to be undertaken by a commercial entity.

Production of the nanocomposite material in quantities large enough to produce materials suitable for flammability testing is desired. Academic or commercial partners are being sought to pursue that goal.

More complete physical testing of the nanocomposites to better determine changes in modulus of elasticity and strength is being pursued. Work was underway to test the physical properties of the nanocomposite fibers when Hurricane Katrina struck the Gulf Coast and damaged both the equipment and materials being utilized in those trials. Preliminary data was recovered and is reported in Chapter 6. The preliminary data is insufficient to draw firm conclusions, but does show promise for considerable improvements in strength. The dry-jet wet fiber spinning system does allow for the physical properties of the regenerated fiber to be

engineered to meet desired goals. Tension control, fiber diameter, and fiber cross-section may be altered to produce the desired physical improvements to the fiber, in addition to the benefits derived from the particulate reinforcement.

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APPENDIX A: STEP-BY-STEP NONWOVEN FORMATION



Figure A.1 – Nanocomposite and Water Slurry in Blender



Figure A.2 – Sheet Mold in Open Position



Figure A.3 – Slurry Poured Into Sheet Mold



Figure A.4 – Raw Sheet and Substrate



Figure A.5 Raw Sheet Ready for Consolidation



Figure A.6 Excess Water Removal



Figure A.7 Wet Consolidated Nonwoven



Figure A.8 Finished Nonwoven Ready for Removal

APPENDIX B: US PATENT NO. 6,893,492, NANOCOMPOSITES OF CELLULOSE AND CLAY



US006893492B2

(12) **United States Patent**
White et al.

(10) **Patent No.:** **US 6,893,492 B2**

(45) **Date of Patent:** **May 17, 2005**

(54) **NANOCOMPOSITES OF CELLULOSE AND CLAY**

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(58) **Field of Search** 106/164.3, 164.51,
106/200.1, 200.2, 200.3, 204.3

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(57) **ABSTRACT**

This invention relates to a process of forming a nanocomposite of cellulose with a clay material that is used as the nanofiller material. The nanocomposites show significant improvements in thermal properties when compared to unbleached cotton and cotton processed under conditions for nanocomposite preparation. The degradation temperature of these nanocomposites is significantly increased over that of unbleached cotton.

13 Claims, No Drawings

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NANOCOMPOSITES OF CELLULOSE AND CLAY

FIELD OF THE INVENTION

The present invention relates to improved thermal stability of nanocomposites made from cellulosic materials in combination with clays such as smectic clays, hectorites and synthetic clays to produce materials that have a raised temperature at which degradation occurs and enhanced char yields.

DESCRIPTION OF THE PRIOR ART

The creation of nanocomposites from a combination of clays and different polymers, which are mixed when they are in the monomeric form, such as polyvinyl chloride, polypropylene, polymethyl methacrylate and polystyrene is known in the art. The prior art teaches that nylon 6-clay nanocomposites have enhanced tensile strength, an enhanced tensile modulus and a higher heat distortion temperature as compared to virgin nylon (Wang et al., Polymer Preprints 42(2), 842-843; 2001).

The creation of polypropylene/clay nanocomposites is taught by Ma et al. (Journal of Applied Polymer Science, Vol. 82, 3611-3617; 2001). With these composites the maximum decomposition temperature increased by 44° C. with the introduction of 10 wt. % clay.

Zeng et al. (Macromolecules 2001, 34, 4098-4103) discloses poly (methyl methacrylate) and polystyrene can substantially improve the dimensional stability of the polymer matrix in an exfoliated nanocomposite with uniform mesoscale clay dispersion.

Hiroyuki Matsumura and Wolfgang Glasser (Journal of Applied Polymer Science, Vol. 78, 2254-2261; 2000) have discovered that by reacting wood pulp fibers in a solvent medium that does not fully penetrate the fibers, and then hot-pressing the modified fibers at elevated temperature they were able to form a semi-transparent polymer sheet that is a nanocomposite of cellulose esters and unmodified cellulose.

Presently, no technique is available for the incorporation of clays in cellulose. A major drawback of cotton is its inherent ability to burn. Flame resistance can be imparted to cotton by conventional processes, but these finishes tend to be subject to loss after laundering and or problems with the fabric holding up to wear. There remains a need for the creation of alternate viable and cost-effective technologies to modify and make better industrial use of cotton fibers and cellulose in general which are available in abundance.

SUMMARY OF THE INVENTION

The present invention relates to the development of improved thermal stability of nanocomposites made from cellulosic materials in combination with smectic clays, hectorites or synthetic clays with a negative charge to produce materials that have increased degradation temperatures and enhanced char yields. Enhanced char yields are a significant identifier of nonflammable material. We have found that cellulose, including cotton, may be dissolved with a solvent and then intimately mixed with a clay at a molecular level. This mixing results in the creation of nanocomposites wherein the clay substituent mixes with the cellulose polymer and becomes incorporated into its matrix upon drying and removal of the solvent. The resultant nanocomposite materials may be used to produce fibers with enhanced flame retardant properties.

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In accordance with this discovery, it is an object of the invention to provide a means for the creation of nanopolymers from cellulose in admixture with clays for the purpose of enhancing fire retardant properties.

Another object is to provide a means for coating materials using the created nanopolymers with enhanced properties for the purpose of fire retardance.

Other objects and advantages of the invention will become readily apparent from the ensuing description.

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves the creation of enhanced thermal stability properties for cellulosic materials such as fibers from bast e.g. flax, kozo and kenaf; wood fibers, leaf fibers e.g. sisal, henequen and abaca; and grass fibers (bamboo and rice straw, bagasse; cotton fiber) and previously processed cellulose fibers such as paper, newspaper or cardboard.

The invention relates to the creation of cellulose-based materials having an increased range of temperatures they will tolerate before undergoing degradation, and the ability of these materials to create high levels of char yield, which is used as a factor to determine level of flammability, as compared to untreated material.

It has been found that cellulosic materials treated with clays such as smectic clays, hectorites and synthetic clays produce materials that have increased degradation temperatures and enhanced char yields. The synthetic clays should have a negative surface charge and be regarded as hydrophobic colloids. Examples of usable synthetic clays are laponite, cloisite, fluorohectorite, hydrotalcite and hematite. Preferred clays are clays of the smectic class. Types of smectic clays include alietite, beidellite, hectorite, montmorillonite, nontronite, saponite, sauconite, stevensite, swinefordite, volkonskoite, yakhontovite, and zincsilite. The nanocomposites produced contain clay at a level of 0.5%-25% of the cellulose/clay composition, with a preferred range being 5%-15% and a most preferred range of 7%-10%.

We have found that cellulose, including cotton, may be totally or partially dissolved with a solvent and then have a clay, such as a smectic clay, hectorite or a synthetic clay mixed with it. Partial dissolution is defined as being a minimum of 50% by weight of the cellulose dissolved. This mixing results in the creation of nanocomposites wherein the clay substituent mixes with the cellulose polymer and becomes incorporated into its matrix upon drying and removal of the solvent. This forms the basis of creating fibers with enhanced flame retardant properties.

Combination Parameters

The clay is required to be pretreated with an ammonium salt or acid that possesses alkylammonium cations or arylammonium cations such as first, second, third degree salts and quaternary compounds preferred compounds include dodecylamine, 12-aminododecanoic acid, or n-decyltrimethyl ammonium chloride alkyl ammonium salts. The resultant pretreated clay is suspended in water. Appropriate concentrations of the alkyl or aryl ammonium cations in water range from 0.005 M to 0.2 M for treating from 1 to 15 grams of clay. This pretreated clay suspension is then dried. The dried clay and the cellulosic material are then combined (with the order of combination not being critical) with a polar aprotic solvent such as 4-methylmorpholine-N-oxide (MMNO), cupriethylenediamine hydroxide, saturated zinc chloride, calcium thioc-

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anate and lithium chloride/dimethyl acetamide with the concentration of the solvent used being dependent upon the amount of cellulosic material to be dissolved. By way of example, for cotton cellulose a ratio of about 50 ml of MMNO per gram of cotton cellulose is preferred, while, for other cellulose and alternate solvent systems the ratio may range from about 10 ml to about 500 ml per gram of material. The amount of clay combined with the cellulosic material should be sufficient to provide a dried cellulose/clay nanocomposite having between 0.5%–25% clay by weight, preferably between 5%–15, and most preferably between 7%–10%.

This cellulose/clay/solvent mixture typically is then heated and refluxed at a temperature ranging from about 100° C. to 150° C. until a suitable amount of the cellulose material is dissolved and the clay is suspended. Approximately 1 hour to 3 hours after reflux is initiated the cellulosic material should be dissolved. If less than total dissolution of the cellulose is necessary then the amount of time involved in this step can be reduced accordingly. Cellulosic fibers from cotton take the greatest amount of time to dissolve due to the nature of its highly crystalline structure and its inherently high molecular weight. Cellulosic material from sources other than cotton fiber will dissolve more readily because of their lacking either or both of these properties. The resultant viscous amber solution is then removed from heat and precipitated in acetonitrile or any other polar solvent that is miscible with the solvent system utilized. The cellulose/clay nanocomposite precipitate may then be dried and collected. The material is preferably filtered and washed in water. The determination of filter and wash parameters are within the skill of the ordinary artisan.

The material is preferably washed and filtered 1 to 5 times, preferably 2–3 times. The cellulosic material is collected and dried under conditions that will not degrade the material so as to make it unusable. Temperatures up to the degradation temperature of cellulose are usable, but temperatures under 175° C. are preferred.

The process of the invention does not require that the clay and the cellulose be added to the solvent solution in a particular sequence. Thus, the order of combination described above can be reversed or carried out simultaneously by whatever means is available to the skilled artisan.

EXAMPLE 1

Cotton nanocomposites containing 0%–15% montmorillonite clay as filler material were prepared in batches of 1–2 grams of material according to the following procedures. Montmorillonite K10 clay (Aldrich Chemical Company, Milwaukee, Wis.) was pretreated with the ammonium salt of dodecylamine according to a previously published procedure (K. Yano, A. Usuki, A. Okada, T. Kurauchi, O. Kamigaito; Journal Polymer Science, Part A: Polymer Chemistry, 31, 2493, 1993). The pretreated clay was then used in the following procedure. Pretreated montmorillonite clay was stirred rapidly in MMNO. After 30 minutes of stirring, cotton was added to the flask. The cotton/clay/MMNO solution was heated to reflux with continued stirring. Approximately 1 hour after reaching reflux, the cotton dissolved.

The viscous amber colored solution was removed from heat and reprecipitated into acetonitrile. The material was filtered and washed a second time in acetonitrile. After filtration, the material was washed in deionized water. After the final wash and filtration, the samples were collected as a powder and dried under vacuum at 120° C.

Thermogravimetric analyses (TGA) were performed on a TA Instruments Hi-Res TGA 2950. Samples were heated to

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120° C. and held isothermally for 1 hour to normalize for moisture content. After air-cooling, scans were run from 40° C. to 600° C. at a heating of 10° C./min. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 821. Thermal analysis results are shown in Table 1.

TABLE 1

Sample (wt % clay)	T _{dec} (° C.)	Char yield (%)
0	326	3
1	327	8
2	331	12
3	327	13
7	327	28
10	321	30
15	316	34

EXAMPLE 2

Following the protocols of Example 1, nanocomposite formulations were prepared using kenaf, ramie; and wood pulp as the source of cellulose. Pretreated montmorillonite clay or cloisite clay (a natural montmorillonite modified with a quarternary ammonium salt) (Southern Clay Products, Inc., Gonzales, Tex.) was used as the filler material. The cellulosic fibers were soaked in MMNO prior to heating to allow wetting of the fiber by the solvent. Thermal analysis results are presented in Table 2.

TABLE 2

		T _{dec} (° C.)	Char yield (%)
Cotton	control	282	3
	montmorillonite	327	28
	cloisite	311	23
Ramie	control	290	16
	montmorillonite	335	32
	cloisite	313	27
Kenaf	control	283	12
	montmorillonite	321	25
	cloisite	305	22
Wood	control	284	13
	montmorillonite	313	25
	cloisite	300	21

EXAMPLE 3

A nanocomposite formulation of 93% cotton and 7% montmorillonite clay was prepared. The mixture was stirred in an open container with heat until cellulose dissolution occurred. Using an automated syringe pump (Pump model 210, KD Scientific, New Hope, Pa.) the viscous dope was extruded from syringes through an 18½ gauge needle at pump speeds varying from 1 mL/min to 10 mL/min. The fibers were spun into an open bath of either acetonitrile or water.

The coagulated fibers were collected manually and washed with water. Both solvents resulted in the removal of MMNO to allow coagulation of the regenerated cellulose and produced nanocomposites in the form of fibers or films. These resultant fibers and films were then dried. The materials were then tested for thermal properties. Thermal decomposition temperature for the materials was 333° C. and the char yield was 25%. These results are comparable to those obtained from cotton nanocomposites of similar formulation produced in Examples 1 and 2.

It is understood that the foregoing detailed description is given merely by way of illustration and that modifications

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and variations may be made therein without departing from the spirit and scope of the invention. For example, choice of specific components, their relative proportion and degree of reaction may be readily determined by those skilled in the art without undue experimentation using the teachings hereof. 5

We claim:

1. A composition comprising a cellulose/clay nanocomposite wherein the clay component represents 0.5% to 25% by weight of the nanocomposite.

2. The composition of claim 1 wherein the cellulose is selected from the group consisting of bast fibers, wood fibers, leaf fibers, grass fibers, bagasse, cotton fiber, paper, newspaper and cardboard. 10

3. The composition of claim 1 wherein the clay is selected from the group consisting of smectic clays, hectorites and synthetic clays. 15

4. The composition of claim 3 wherein the clay is a smectic clay.

5. The composition of claim 4 wherein the clay is montmorillonite. 20

6. The composition of claim 1 wherein the clay component represents 5% to 15% by weight of the nanocomposite.

7. The composition of claim 1 wherein the clay component represents 7% to 10% by weight of the nanocomposite.

8. A method of producing a cellulose/clay nanocomposite comprising the steps of: 25

a) providing a clay selected from the group consisting of smectic clays, hectorites and synthetic clays, pretreating the clay with an alkylammonium or an arylammonium cation, and suspending the pretreated clay in water to form a suspension; 30

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b) drying the suspension of step a) to form a dried clay;

c) mixing the dried clay from step b) and a cellulosic material in a cellulose solvent and heating and refluxing the admixture at a temperature ranging from about 100° C. to 150° C. for a period of time sufficient to suspend the clay and partially or completely dissolve the cellulose;

d) precipitating the product of step c) in a polar solvent that is miscible with said cellulose to form of a cellulose/clay composite; and

e) collecting and drying the reprecipitated cellulosic/clay material.

9. The method of claim 8 wherein the clay is a smectic clay.

10. The method of claim 9 wherein the smectic clay is montmorillonite.

11. The method of claim 8 wherein the clay is pretreated with an ammonium salt selected from the group consisting of dodecylamine, 12-aminododecanoic acid and n-decyltrimethyl ammonium chloride alkyl ammonium salts.

12. The method of claim 8 wherein the cellulosic material is selected from the group consisting of bast fibers, wood fibers, leaf fibers, grass fibers, bagasse, cotton fiber, paper, newspaper and cardboard.

13. The method of claim 12 wherein the cellulosic fiber is either wood fibers cotton fibers.

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VITA

Christopher Delhom is a native of New Orleans, Louisiana. Chris is a graduate of the University of New Orleans, Department of Mechanical Engineering. Chris began his graduate studies at Louisiana State University part-time in 2001, while working as a support scientist for the United States Department of Agriculture's Agricultural Research Service in New Orleans, Louisiana, before being interrupted by Hurricane Katrina in 2005. Chris is currently a research scientist for the Agricultural Research Service in New Orleans, Louisiana, after working in Stoneville, Mississippi, and Clemson, South Carolina, for the Agricultural Research Service. His technical interests are in material properties and machine design with emphasis on improving the processing efficiency and measurement of quality of cotton fibers.